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THE EFFECT OF ALUMINUM ON URANIUM BIOSORPTION BY IMMOBILIZED RHIZOPUS ARRHIZUS

FINAL REPORT

by

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CANADA

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EXECUTIVE SUMMARY

Uranium competitve equilibrium uptake isotherms by **Rhizopus arrhizus** were determined at three different solution pH levels and in the presence of different concentrations of competiting ions, namely aluminum, iron and thorium. The co-ion effect became more pronounced as the co-ion concentration in solution and pH level increased. A preliminary examination of the effect of aluminum on the rate of uranium uptake was also completed. Results showed that the presence of aluminum does not interfere with the kinetics of uranium uptake by **Rhizopus arrhizus**. Electron microscopic and EDAX x-ray analysis were also performed on samples of the biomass. The combination of spectral data and the information from both the equilibrium studies and the kinetic studies suggested that aluminum interferes with the uranium biosorptive uptake capacity of **Rhizopus arrhizus** by the precipitation of a metastable amorphous hydroxy polymeric precipitate.

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THE EFFECT OF ALUMINUM ON URANIUM BIOSORPTION BY IMMOBILIZED RHIZOPUS ARRHIZUS

1. INTRODUCTION

1.1 Project Scope and Objectives

Recent work at McMaster, jointly funded by McMaster and CANMET has shown that aluminum can effectively suppress the uranium uptake capacity of the immobilized microbial biomass[1]. Results from a pilot plant observed at CANMET on the continuous recovery of uranium from the Denison Mine bioleach solutions have confirmed this observation. It is therefore important to try and understand the mechanism by which aluminum reduces the biomass uranium uptake capacity. Then we can attempt to devise ways to eliminate this interference so as to maintain the maximum possible uranium uptake capacity. This will improve significantly the economics of the new technology. This report is the final report for DSS contract number 23440-9-9019/01-SS.

The underlying focus of this project was to complete a detailed and systematic study of the effects of aluminum on uranium biosorption. The following detailed objectives were established:

1. Detailed biosorption equilibrium studies to quantify the effect of aluminum competition effect.
2. Examination of the effect of pH on the competition effect of aluminum on the biosorption equilibrium.
3. Preliminary examination of the effect of aluminum on the kinetics of uranium uptake.
4. Detailed Electron Microscopic and microprobe analysis of the sites of aluminum in the immobilized biomass particle with respect to uranium. Use (if possible) of IR spectroscopy.
5. Critical assessment of the information and development of a hypothesis to explain the competition mechanism.

6. Proposal of possible countermeasures to counteract the aluminum competing ion effect.

The first and second objectives were accomplished by growing the R.arrhizus biomass and then carrying out a series of batch equilibrium biosorption tests to develop biosorption isotherms using raw biomass with different process solutions at different pH values. The effect of aluminum on the kinetics of the uranium biosorption process were examined using a batch reactor with non-immobilized biomass. Different solutions of uranium and aluminum were tested. The fourth objective was accomplished by analyzing both immobilized biomass that had been used in the Denison Mine pilot plant as well as the biomass that had been used in the adsorption isotherm studies. Based on the results from the first four objectives, the fifth objective was then accomplished. From the results from the fifth objective, the sixth objective proved unnecessary.

2. MATERIALS AND METHODS

2.1 Biosorbent Production

A strain of **Rhizopus arrhizus** has been maintained in a morphogically stable form was used as the inoculum. The biomass was then grown, in a twin 14 L bench top fermenter (New Brunswick Scientific, MF 214, New Jersey), in a peptone-glucose medium under carefully controlled conditions. Sterile conditions were maintained to prevent contamination by other microorganisms. Once growth was complete the contents of the vessels were filtered through bags of nylon mesh. The recovered biomass was then washed extensively with tap water. The washed biomass was then lyophilized in a (Virtis Model No. 10-100) freeze drier. The resulting freeze dried biomass is hard and light brown in colour. It was then sized by grinding through sieves to the desired size fraction and then immobilized using the proprietary spouted bed system developed at McMaster University[2,3].

Several batches of biomass were produced and tested to compare the uranium uptake between batches. The uranium uptake of the different batches of biomass was examined before and after immobilization and was found to be consistent.

2.2 Solutions

All solutions used in these experiments were made using analytical grade chemicals and distilled deionized water. Uranyl nitrate and thorium nitrate crystals were purchased from BDH Chemicals Ltd. and aluminum nitrate and ferrous chloride crystals were purchased from Fisher Scientific. The synthetic solutions were made up by dissolving the salts in distilled deionized water and then adjusting the pH (using either NaOH or HNO_3) to the desired value. The pH adjusted solution was then allowed to sit for at least one hour. The pH was then rechecked and adjusted, if necessary.

2.3 Competitive Adsorption Isotherms

Biosorption equilibrium isotherms were determined by contacting varying quantities of raw biomass with a given volume of the process solution and allowing the system to reach equilibrium. Measured quantities of biomass were placed in 250 mL screw top flasks with 100 mL of process solution. The flasks were agitated on an orbital shaker for 24 hrs to allow each system to reach equilibrium. The biomass was then separated from the liquid phase by filtering through a 0.45 μm membrane filter. The filtrates were collected for analysis. The biomass collected on the filters was washed with distilled water to remove any residual solution and recovered for analysis. All solutions were analyzed using an ICP spectrophotometer. A precision analysis is given in Appendix 1.

2.4 Biosorption Kinetics

The rate of the biosorption process and the effect of aluminum on this rate, was determined using a Carberry reactor (Figure 2.1). A measured quantity of immobilized biomass was placed in the rotating cage which was filled with 2 L of process solution. Using a 10 cc syringe, 3 mL samples were periodically withdrawn from the reactor. Two mL samples were used for analysis. The solution temperature was controlled at 23 °C +/- 1 °C by regulating the flow rate of cooling water through the reactor jacket. The sorption rate at different mixing speeds was examined earlier and it

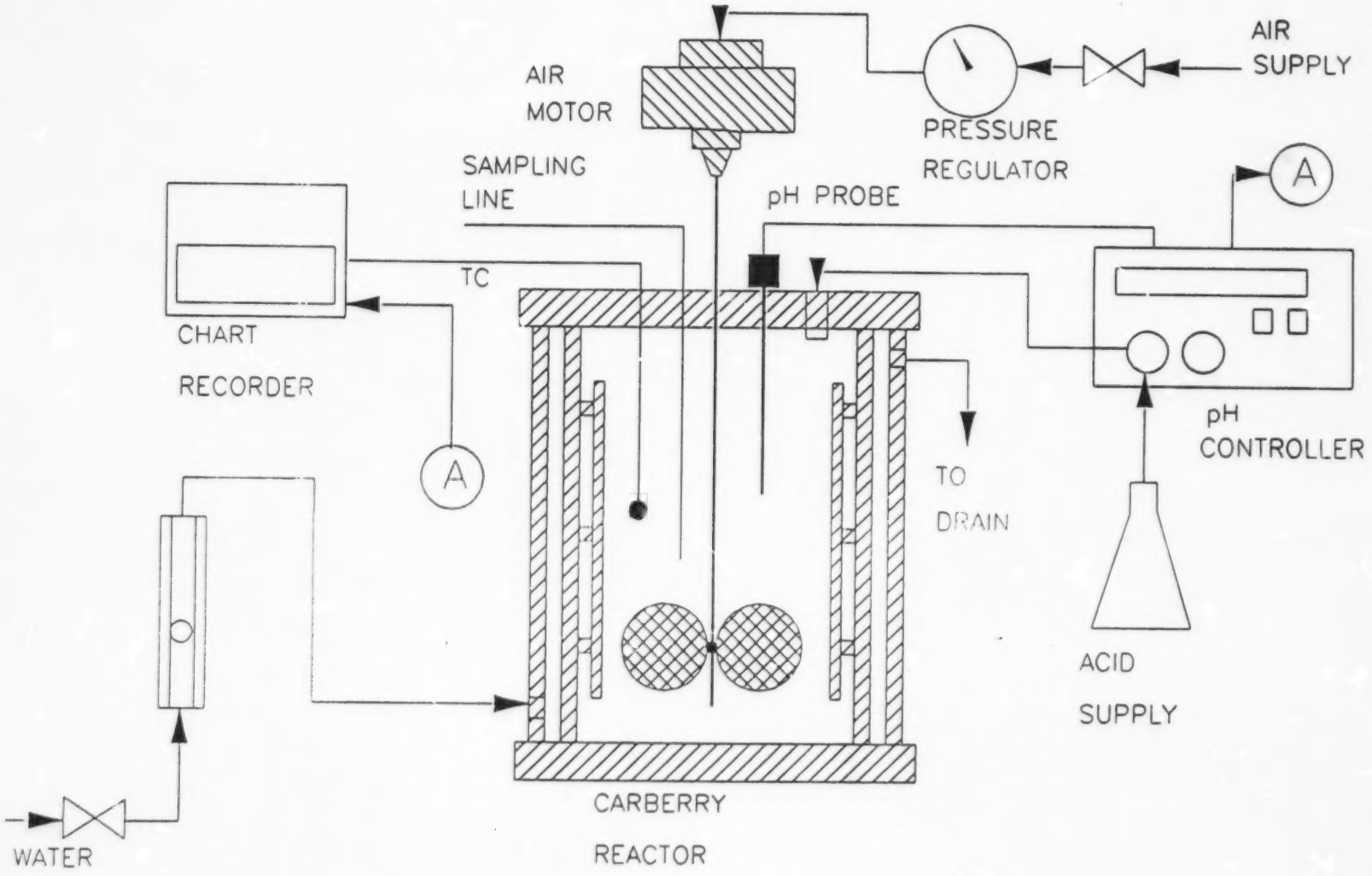


Figure 2.1 Biosorption Kinetics Experimental System

was determined that the mass transfer in the bulk solution had no effect on the observed sorption kinetics[4]. Hence, the observed biosorption rates are the intrinsic rates, independent of mixing intensity in the reactor. All solutions used were synthetic; uranyl nitrate solutions with varying concentrations of aluminum nitrate.

2.5 Transmission Electron Microscopy

Transmission electron micrographs were made on a Phillips EM-300 model electron microscope at an accelerating voltage of 40 KV. The immobilized biomass pellets were fixed with a 2.5% solution of glutaraldehyde (E.M. grade), in 0.1 m cacodylate buffer (pH = 7.2) for two days at room temperature. Then they were dehydrated with a series of washes with ethyl alcohol concentrations and embedded in Spurr epoxy resin. Using an LKB Microtome III, sections 800 Å thick were cut. These sections were then mounted on copper grids.

2.6 EDAX X-ray Analysis and Mapping

Using the specimens prepared for transmission electron microscopy, X-ray energy dispersion spectra were recorded. The system consisted of a JEOL JEM-1200 EX electron microscope, and a Tracor Northern X-ray detector unit. The microprobe was focused at a magnification of 100,000 at an 80 KV acceleration voltage.

Digitized map or line scans show the location and relative concentration of elements in the Rhizopus arrhizus cell wall after being exposed to process solutions. The map scan constructs digitized images according to the intensities of x-rays produced by an electron microscope. During each map scan, the number of image pixels are specified according to the resolution required. Each image pixel is assigned an intensity value based on the data from which the image is constructed. For x-ray maps (map scans) the intensities are based on the x-ray count for that portion of the sample. That is, the higher the count rate, the greater the intensity. A map scan is essentially made up of a series of line scans.

3. PRESENTATION OF RESULTS

3.1 Competitive Adsorption Isotherms

Uranium adsorption tests were carried to determine the effect of competing ions on the intrinsic uranium uptake capacity. A series of experiments were run with synthetic solutions of uranyl nitrate and varying dosages of ferric chloride, aluminum nitrate and thorium nitrate. These experiments were also conducted at different pH values; 2,4 and 5. Table 3.1 gives a summary of the biosorption isotherm experiments conducted.

Table 3.1:
Summary of Biosorption Isotherm Experiments

	Initial Concentration, mg/L			
pH	Uranium	Aluminum	Iron	Thorium
2, 4, 5	300	0, 10, 50, 75, 100	0	0
2, 4, 5	300	0	0, 10, 50, 100	0
2, 4, 5	300	50	0, 10, 50, 100	0
2, 4	300	0	0	0, 50, 100, 200
2, 4	300	50	0	0, 50, 100, 200

Table 3.2 presents the percentage changes of uranium uptake at pH = 4 with increasing concentrations of aluminum. At a pH of 4 and constant initial uranium concentration (300 mg/L), the aluminum suppressed the uranium biosorptive uptake capacity of **Rhizopus arrhizus** in direct proportion to the initial aluminum concentration in solution (Figure 3.1).

Table 3.2: Effect of Aluminum on the Uranium Biosorptive Uptake Capacity of R. arrhizus, pH = 4

Aluminum Concentration, mg/L	0	10	25	50	75	100
U Uptake Capacity, mg/g*	168	142	130	126	114	106
% change of U Uptake	-	15	23	25	32	37

* C_{eq} = 160 mg/L

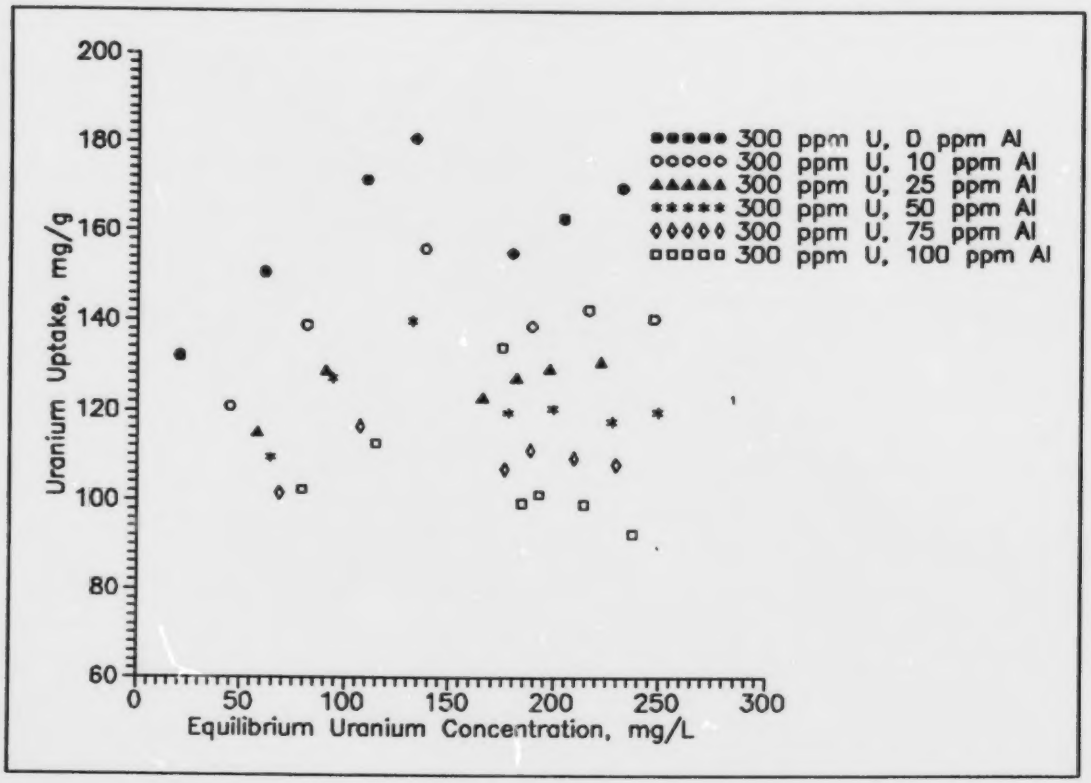


Figure 3.1: Effect of Aluminum on Uranium Biosorption, pH = 4

The effect of iron on the uranium biosorptive capacity at a pH of 4 and an initial uranium concentration of 300 mg/L is shown in Figure 3.2. At a low iron concentration (10 mg/L), the presence of iron has little effect. However, as the concentration of iron increases, the uranium uptake capacity is reduced, but the isotherms at the higher iron concentration do not remain relatively flat as in the U-Al system, but increase as the equilibrium uranium concentration increases. A copper coloured precipitate and a yellow gel were noticed on the filter paper, with the biomass after filtering. At a pH of 4, iron is characterized by low solubility and will precipitate out of solution, and it appears that uranium is precipitating out of solution as well. The chemistry of the U-Fe system will be discussed further in Section 4.

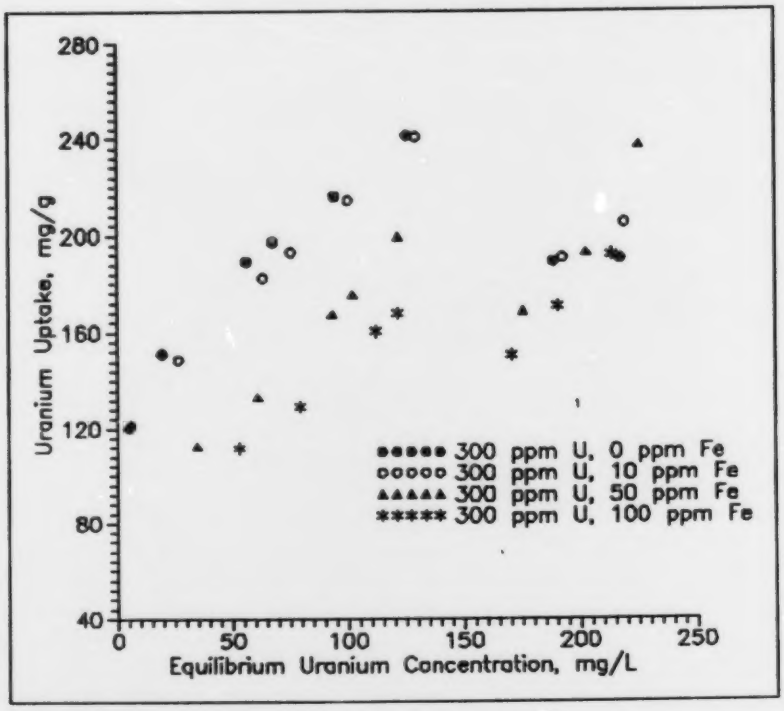


Figure 3.2: Effect of Iron on Uranium Biosorption, pH = 4.

The effect of both iron and aluminum on the uranium biosorptive capacity at a pH of 4 is shown in Figure 3.3. For this series of experiments, the pH of the U-Al-Fe system increased as the concentration of iron increased. That is, for the initial concentration of iron = 50 mg/L and 100 mg/L, the final pH of the solution was observed to be 4.2. This increase in pH was not observed in either the U-Al system or the U-Fe system. With a change in pH the solubility of the solution will change (in this case decrease).

Figure 3.4 shows the effect of increasing amounts of thorium on the uranium biosorptive capacity at a pH of 4. At low initial concentrations of thorium the uranium biosorptive is not affected. However, with initial thorium concentrations of 100 and 200 mg/L, at high equilibrium uranium concentrations, the solution will precipitate. At low equilibrium uranium concentrations, the uranium biosorptive capacity does not appear to be affected. Thorium chemistry will be discussed later.

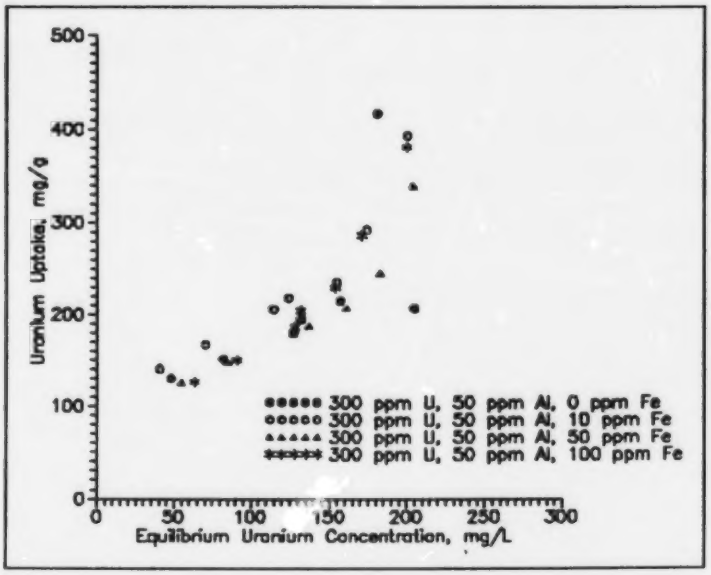


Figure 3.3: Effect of Aluminum and Iron on Uranium Biosorption, pH = 4.

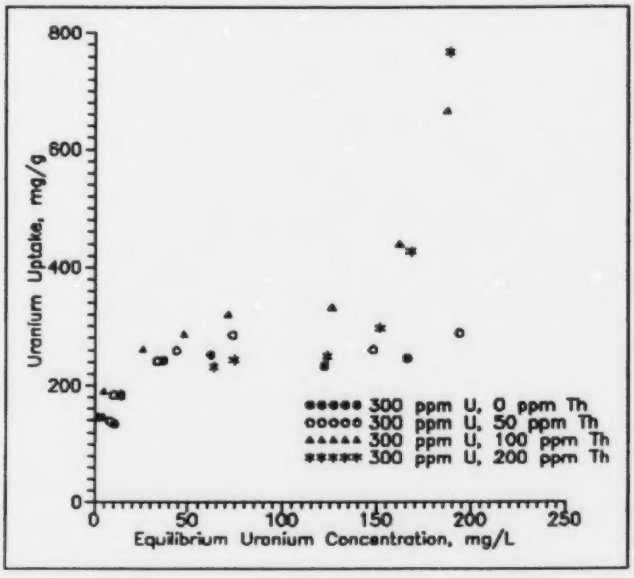


Figure 3.4: Effect of Thorium on Uranium Biosorption, pH = 4.

For the U-Al-Th system (Figure 3.5) the uranium biosorptive capacity is not affected until the initial thorium concentration reaches 200 mg/L. As in the U-Th system, at this pH thorium will precipitate, likely removing uranium from the system. The pH in this system drifted downwards, towards a final pH of 3.8.

The effect aluminum, iron and thorium have on the uranium biosorptive capacity will be discussed in Section 4, along with the mechanism through which aluminum suppresses the uranium biosorptive capacity of **Rhizopus arrhizus**.

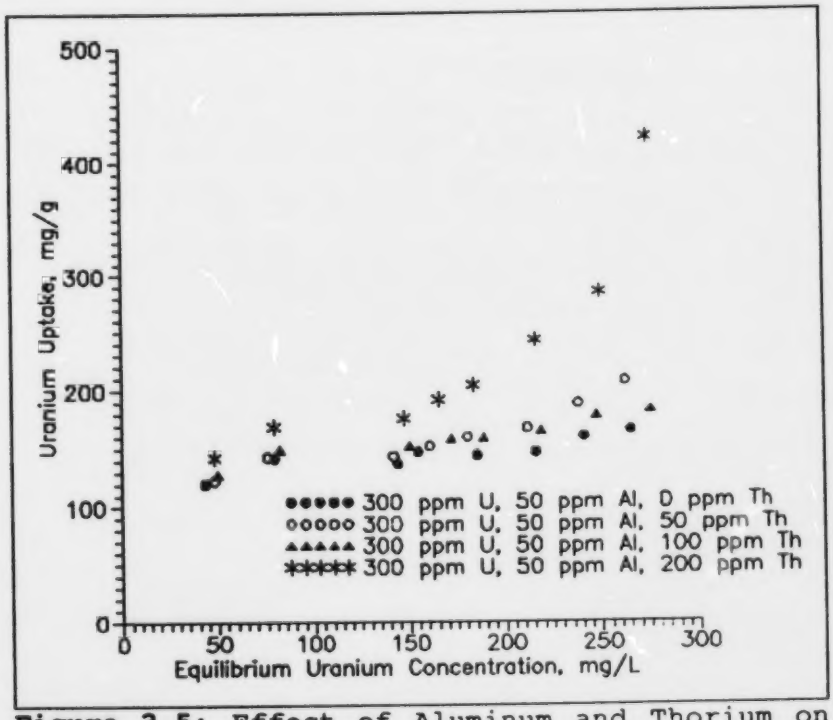


Figure 3.5: Effect of Aluminum and Thorium on Uranium Biosorption, pH = 4.

At a pH of 2 and constant initial uranium concentration (300 mg/L), neither aluminum, iron nor thorium had an appreciable effect on the uranium uptake capacity of **Rhizopus arrhizus**, regardless of the initial co-ion concentrations. Figure 3.6 is a typical isotherm for the uranium-co-ion system at pH = 2. In each experimental system, the pH did not drift, it remained constant at 2.

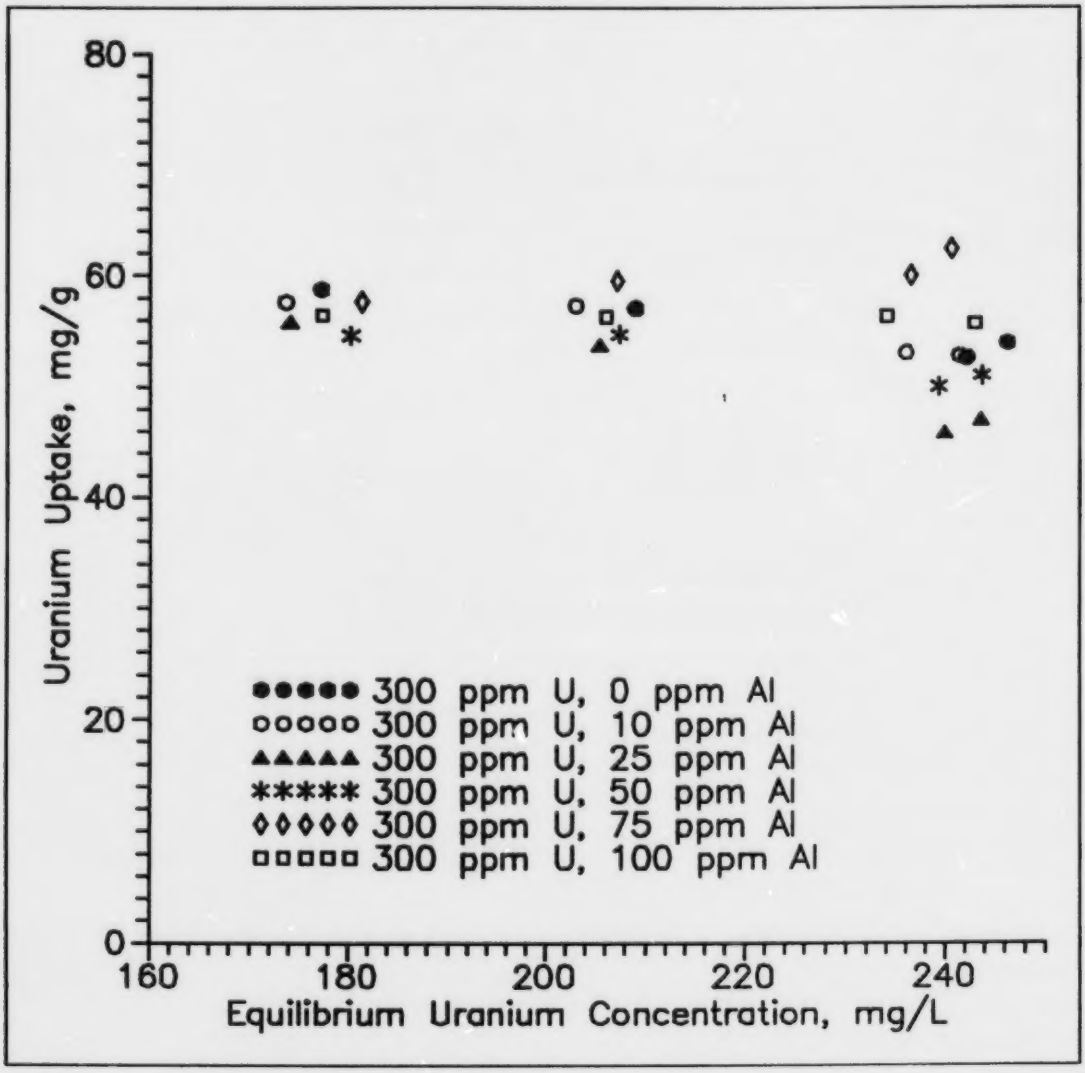


Figure 3.6: Effect of Aluminum on Uranium Biosorption, pH = 2.

At a pH of 5 and constant initial uranium concentration (300 mg/L), the presence of both aluminum and iron resulted in the precipitation of uranium from the system, as in the U-Th and U-Th-Al systems at pH = 4 (Figures 3.7-3.9).

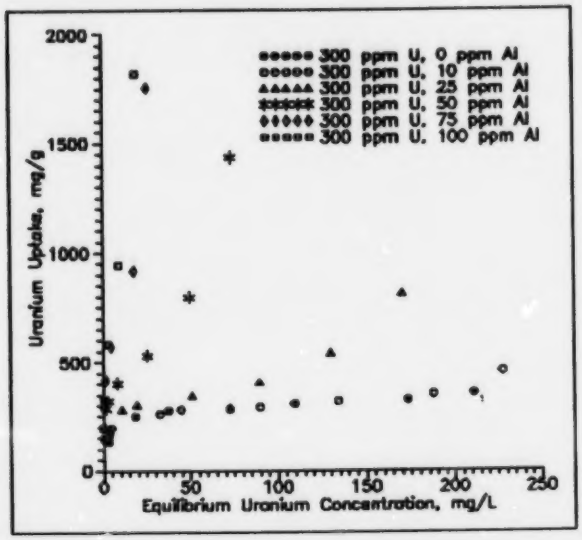


Figure 3.7: Effect of Aluminum on Uranium Biosorption, pH = 5.

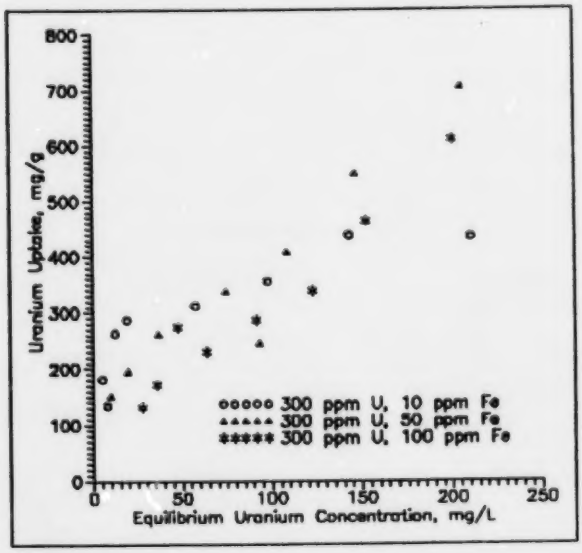


Figure 3.8: Effect of Iron on Uranium Biosorption, pH = 5.

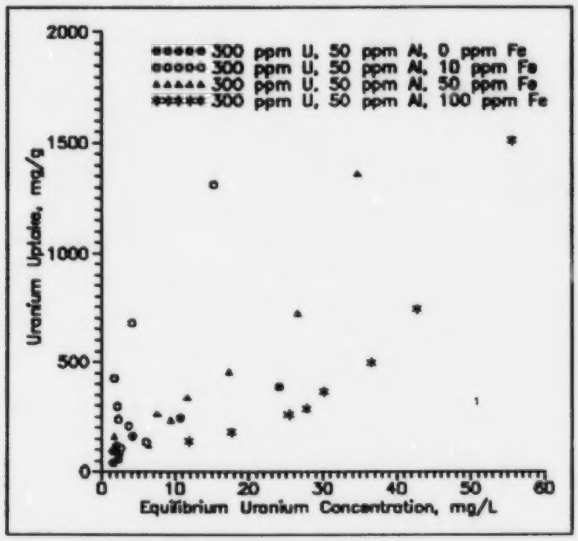


Figure 3.9: Effect of Aluminum and Iron on Uranium Biosorption, pH = 5.

For all experiments the final concentrations of aluminum, iron and thorium were also monitored. The results are tabulated in Appendix 1, along with the corresponding uptake. In the experiments where precipitation did not occur, the results show that the co-ion uptake was relatively low.

3.2 Biosorption Kinetics

A preliminary investigation of the effect of aluminum on the kinetics of uranium uptake by **Rhizopus arrhizus** was determined using a Carberry reactor, as outlined in section 2. A summary of the experiments is shown in Table 3.2.

Table 3.3: Summary of the Kinetic Experiments				
Run	Uranium Concentration, mg/L	Aluminum Concentration, mg/L	Length of run, hours	pH
1	500	0	193	4
2	500	500	199	4
3	500	0	75	4

The results for the first two kinetic experiments are given in Appendix 2, and are shown graphically in Figures 3.10-3.12. For the first experiment (U=500 mg/L) 94 % of the equilibrium loading is achieved in approximately 10 hours. For the second experiment (U=Al=500 mg/L) 92 % of the equilibrium loading is achieved in approximately 10 hours. It appears then, that although the presence of aluminum does result in a reduction of the uranium uptake capacity, it does not appear to slow the rate of the uranium adsorption process at all.

The pH was monitored in all experiments, and the results for the first two experiments are given in Appendix 2. The results are shown graphically in Figure 3.12. As the kinetic run starts, the pH increases, then after the initial rapid adsorption period, drops slowly back down to the original pH. The increase in pH for both experiments peaks in approximately 3.5 hours, with the peak pH value for the uranium only system being 4.20 and for the U-Al system 4.43. This corresponds to approximately 82 % of the equilibrium loading for the U only experiment, and approximately 73 % of the equilibrium loading for the U-Al experiment. After approximately 17 hours, the pH for both experiments had almost returned to the initial pH value of 4.0.

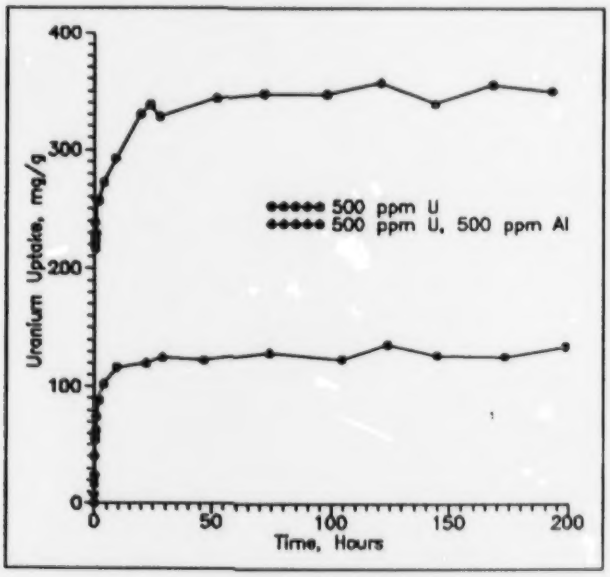


Figure 3.10: Effect of Aluminum on the Kinetics of Uranium

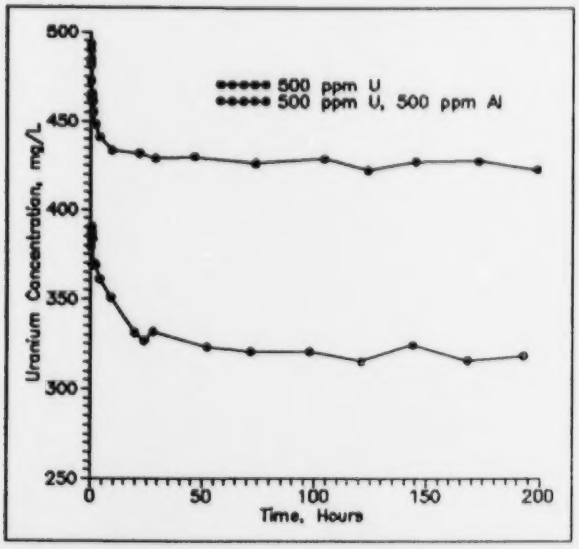


Figure 3.11: Effect of Aluminum on the Kinetics of Uranium Biosorption.

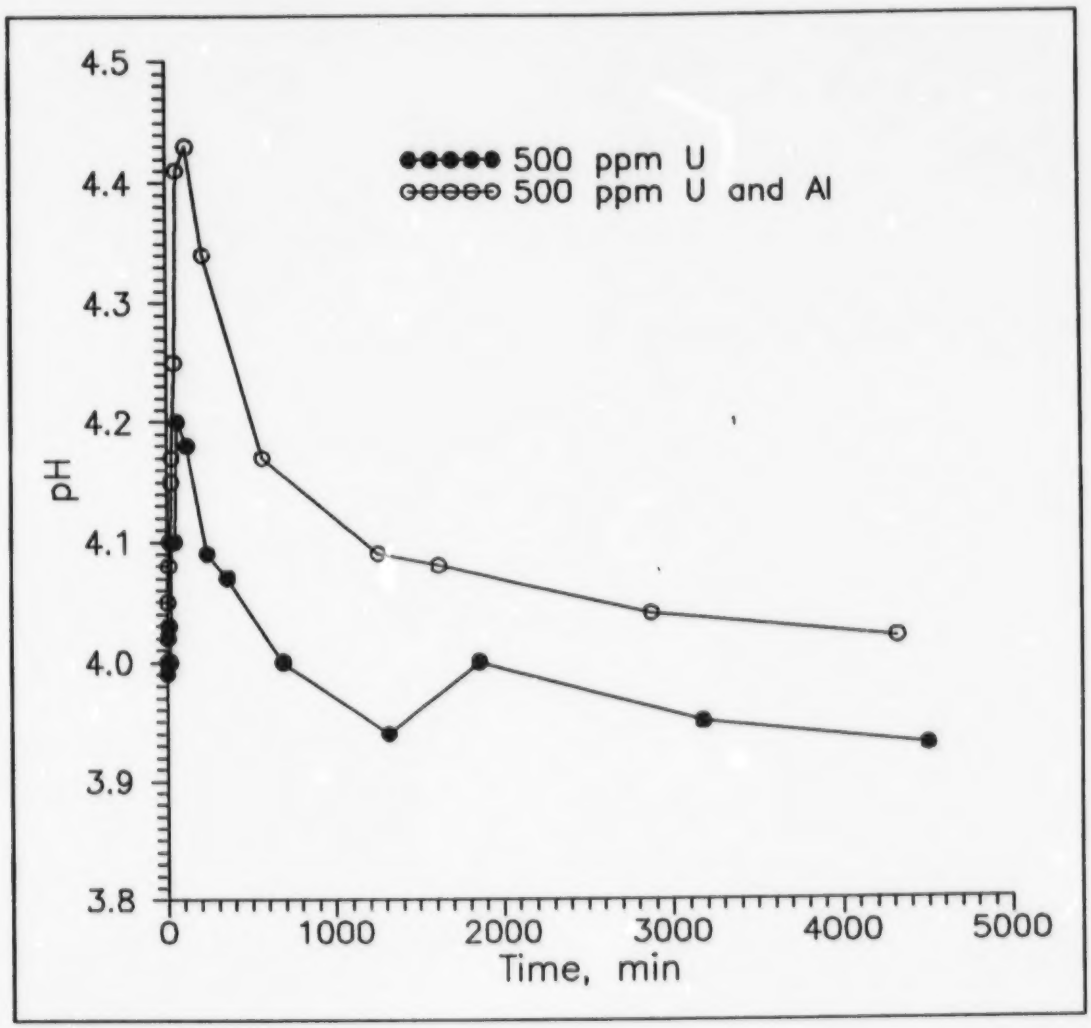


Figure 3.12: pH versus Time for the Kinetic Experiments.

3.3 Electron Microscopy

Transmission electron microscopy, EDAX x-ray analysis and line scans were performed, as outlined in sections 2.5 and 2.6, on two sets of biomass samples; 1) samples from the CANMET pilot plant and 2) samples from the competitive adsorption tests.

3.3.1 CANMET Biomass Samples

Immobilized Rhizopus arrhizus previously exposed to a lengthy series of loading and elution cycles has been analyzed for the presence and distribution of aluminum. The particles analyzed were first grouped according to colour; dark orange, light yellow/orange and beige/white (original colour). Typical results are presented in Figures 3.13 to 3.18. EDAX x-ray analysis shows that for the dark orange particles, thorium and iron are present in significant amounts (Figure 3.14). Line scan analysis shows that the iron and thorium peaks correlate, suggesting a possible relationship between iron and thorium. Uranium and aluminum were not detectable. Figure 3.16 shows typical EDAX x-ray results for the light yellow particles. Again, uranium and aluminum were not detected, but thorium and iron are present in significant amounts. Judging by signal strength the amount of thorium and iron present in the light orange particles appears to be less than that present in the dark orange particles. Figure 3.18 shows typical x-ray results for the beige/white particles. Uranium, aluminum and silica are present in significant amounts, while thorium and iron were not detected.

3.3.2 Biosorption Isotherm Samples

After the equilibrium uptake experiments were completed, biomass samples from each set of experiments were collected for electron microscopic analysis. All samples were washed thoroughly and dried before being prepared for microscopic work, as outlined in Section 2.5 and 2.6.

Figure 3.13:
Typical TEM micrograph of a dark orange CANMET biomass sample.
Magnification = 10 K

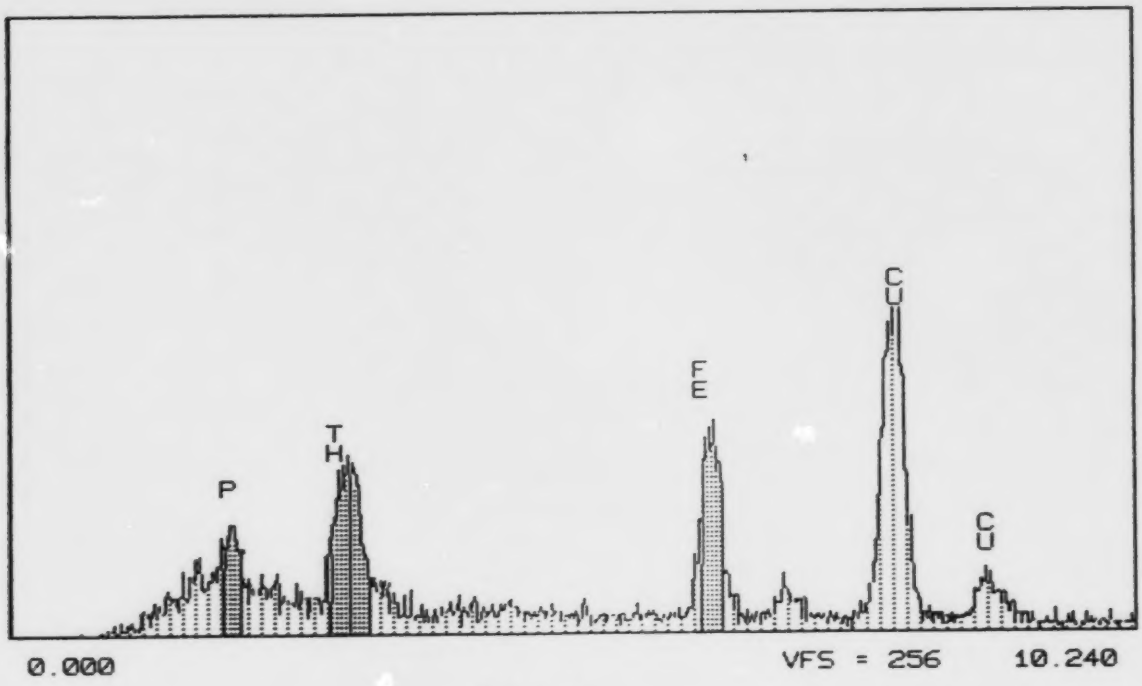


Figure 3.14:
EDAX analysis of a Rhizopus arrhizus cell wall in a dark orange CANMET biomass sample.

Figure 3.15:
Typical TEM micrograph of a yellow/orange CANMET biomass sample.
Magnification = 10 K

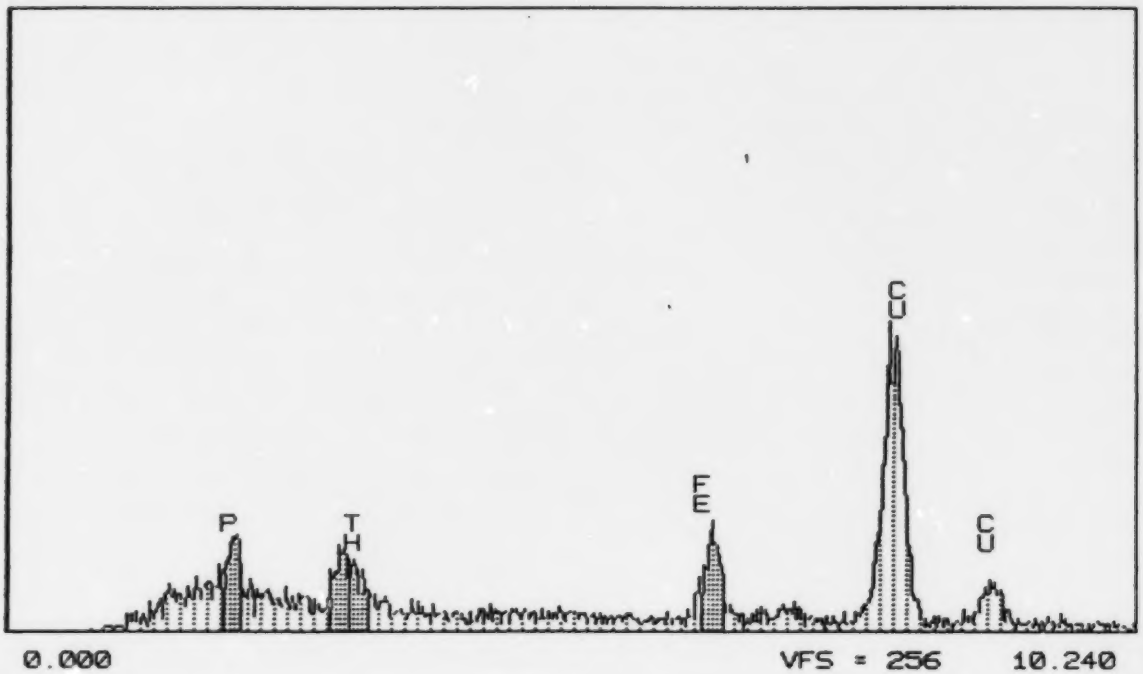


Figure 3.16:
EDAX analysis of a yellow/orange CANMET biomass sample.

Figure 3.17:
Typical TEM micrograph of a beige/white
(original colour) CANMET biomass sample.
Magnification = 10 K

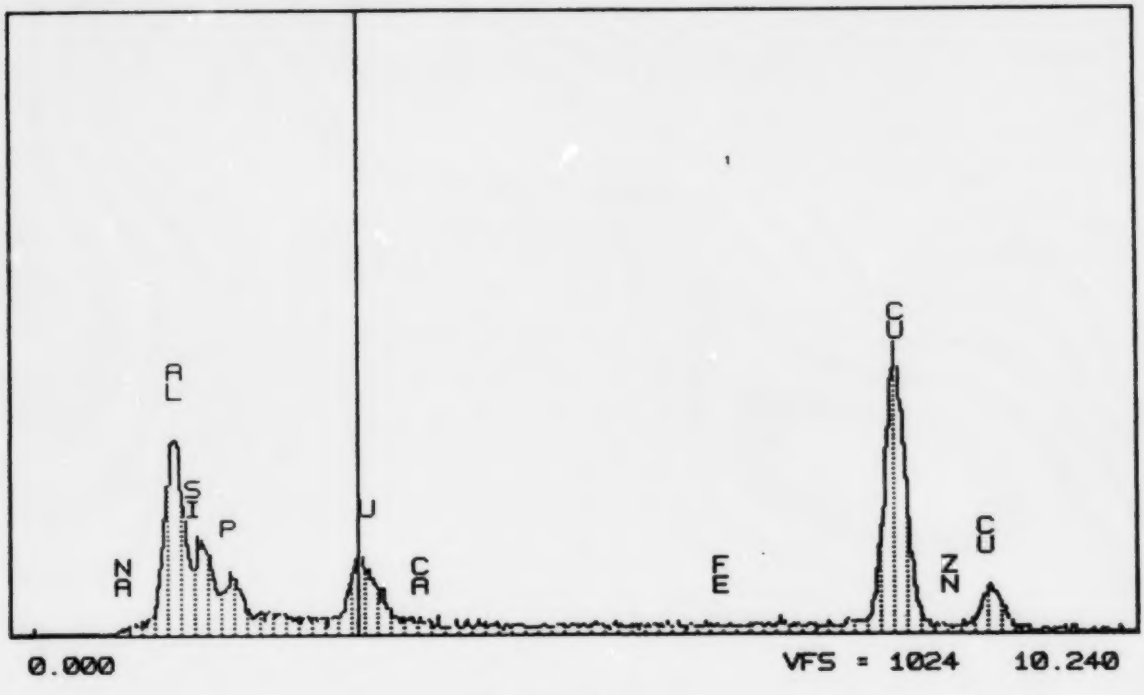


Figure 3.18:
EDAX analysis of a beige/white CANMET biomass sample.

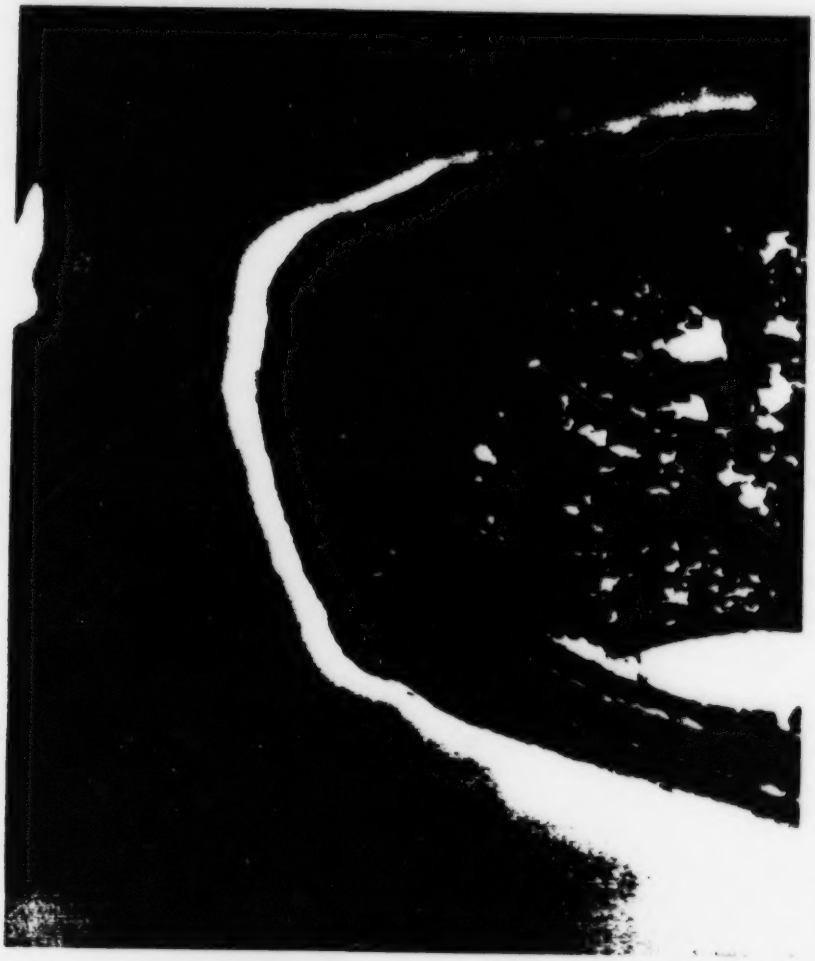
Figure 3.19 is a typical TEM micrograph of **Rhizopus arrhizus** sample after being exposed to uranium and aluminum at pH 4. Note that, as expected, electron dense layers are present only in the cell wall[1]. EDAX analysis of this sample confirms that the dark layers within the cell wall are uranium, with a trace amount of aluminum present (Figure 3.20).

Figure 3.21 is a TEM micrograph of a **Rhizopus arrhizus** cell wall after being exposed to uranium and iron at an initial pH of 4. Note the difference in the location of the electron dense layers, as compared to Figure 3.19. In the U-Fe system, a dark rather fluffy layer appears around the cell wall. EDAX analysis of this layer confirms the presence of uranium and iron (Figure 3.22). Analysis of the lighter layers within the cell wall confirms the presence of uranium, again with trace amounts of iron. The competitive adsorption isotherms indicate that at higher initial iron concentrations, the precipitation of iron and uranium is clearly possible, hence it appears from microscopic analysis that a layer of precipitate coats the outside of the **Rhizopus arrhizus** cell wall, and blocks access to the chitin sites. Cytoplasm analyzed also indicates a strong presence of uranium, confirming that uranium is precipitating.

Figure 3.23 is a typical TEM micrograph of **Rhizopus arrhizus** exposed to a U-Al-Fe solution. As in the U-Fe system, the outer edge of the cell wall appears to be rather fluffy, though the distinct dark outer layer is not visible. Analysis of the cell wall indicates that the electron dense layers contain uranium, with trace amounts of aluminum and iron, throughout (Figure 3.24). The cytoplasm also contains uranium, as in the U-Fe system.

A typical TEM micrograph of **Rhizopus arrhizus** exposed to U-Al and thorium solutions is shown in Figure 3.25. The cell wall is completely dark (electron dense). EDAX analysis confirms a strong presence of uranium and aluminum, but no appearance of thorium (Figure 3.26). These results are similar to the EDAX analysis of the U-Th system; thorium was below detection limits. From the competitive adsorption isotherm tests, the results indicate that thorium must precipitate out of the system without or before adsorbing onto the biomass.

Figure 3.19:
Typical TEM micrograph of a Rhizopus arrhizus sample after being exposed to an aluminum and uranium solution at a pH of 4.
Magnification = 12 K



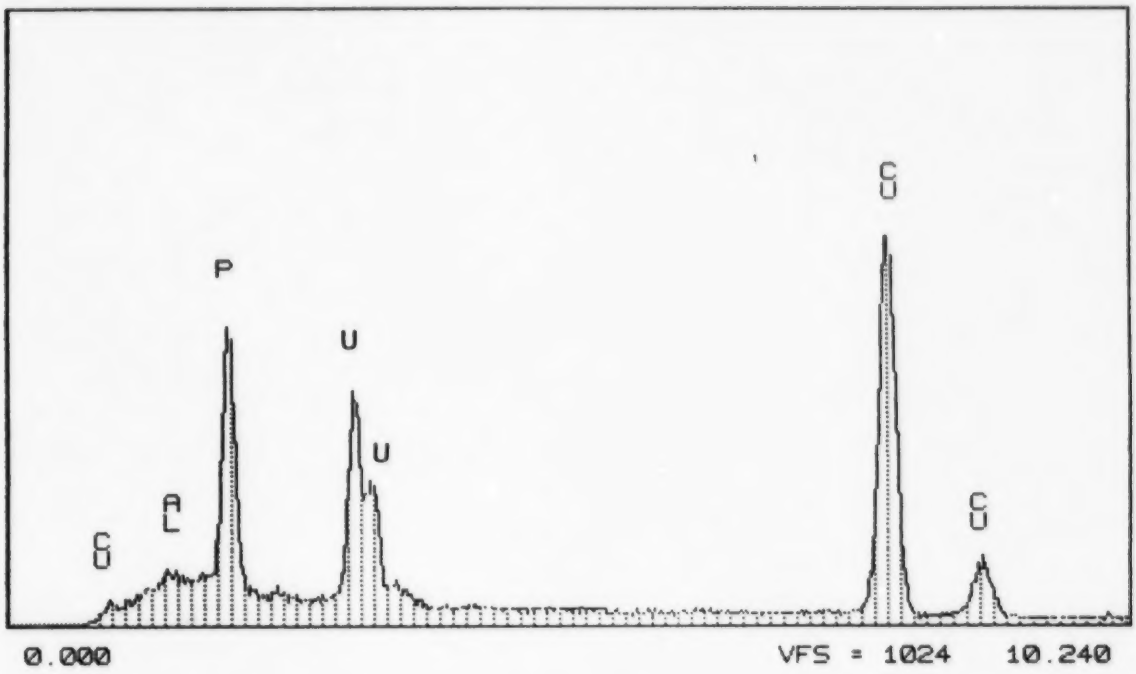


Figure 3.20:
EDAX analysis of a <u>Rhizopus arrhizus</u> after being exposed to an aluminum and uranium solution at a pH of 4.

Figure 3.21:
Typical TEM micrograph of a Rhizopus arrhizus sample after being exposed to an iron and uranium solution at pH = 4.
Magnification = 25 K

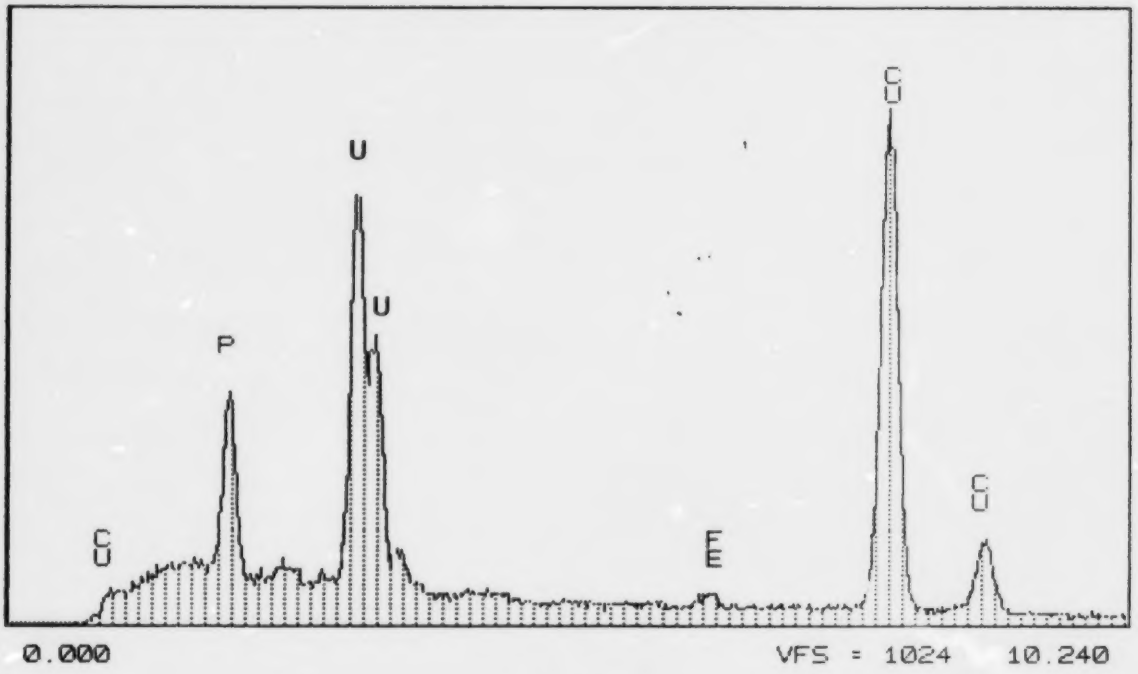


Figure 3.22:
EDAX analysis of a **Rhizopus arrhizus** sample after being exposed to an iron and uranium solution at a pH of 4.

Figure 3.23:
Typical TEM micrograph of a Rhizopus arrhizus sample after being exposed to an aluminum, iron and uranium solution at a pH = 4.
Magnification = 30 K

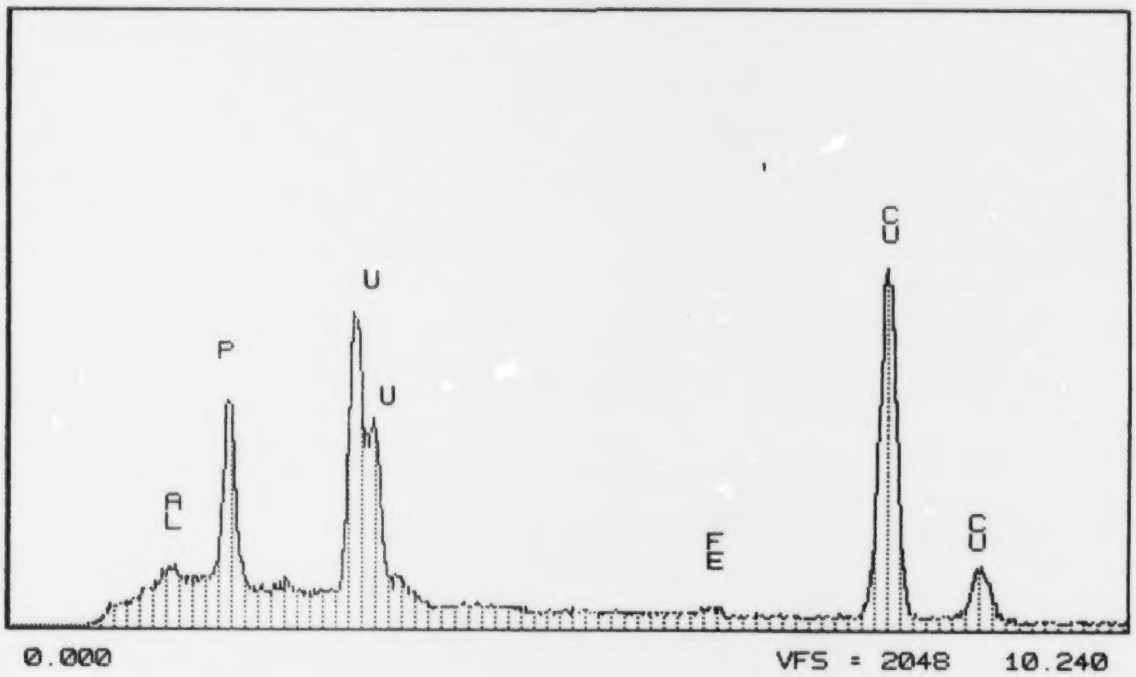


Figure 3.24:
EDAX analysis of a **Rhizopus arrhizus** sample that has been exposed to an iron, aluminum and uranium solution at a pH of 4.

Figure 3.25:
Typical TEM micrograph of a <u>Rhizopus arrhizus</u> sample after being exposed to a thorium, aluminum and uranium solution at a pH = 4. Magnification = 30 K

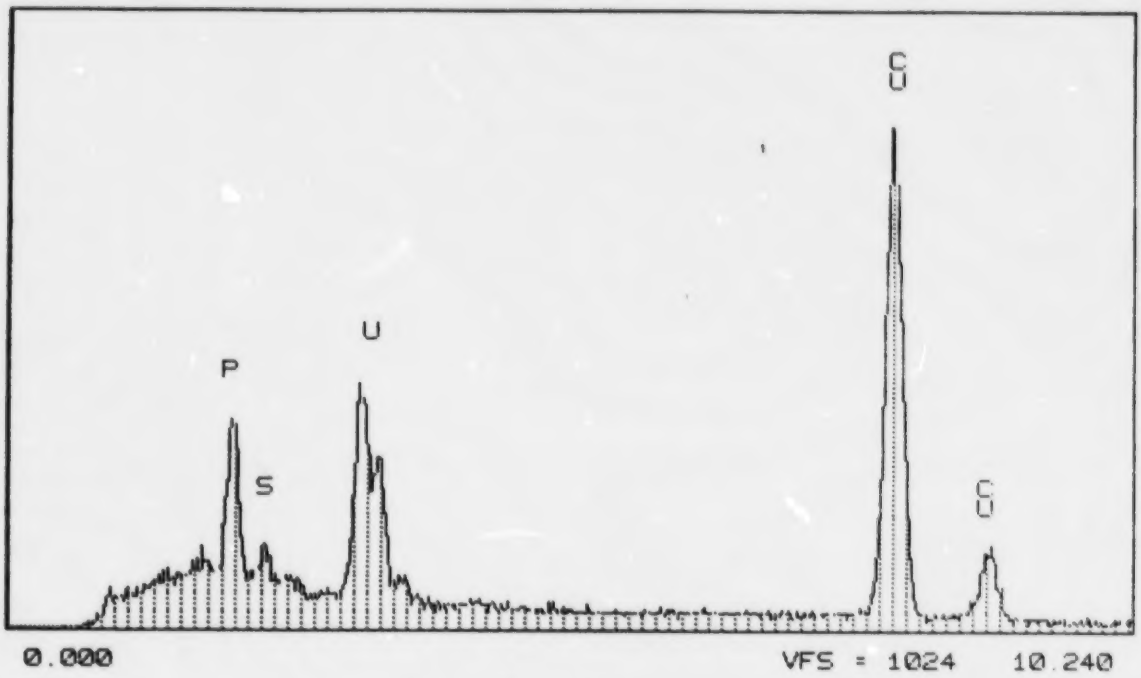


Figure 3.26:
EDAX analysis of a <u>Rhizopus arrhizus</u> sample that has been exposed to a thorium, aluminum and uranium solution at a pH = 4.

4. DISCUSSION OF RESULTS

4.1 Biosorption Isotherms

Competitive biosorption isotherms were carried out to determine the effect aluminum, thorium and iron would have on the intrinsic uranium uptake capacity of Rhizopus arrhizus. The tests were performed using synthetic solutions and at three different pH values; 2,4 and 5.

Before discussing the experimental results, the mechanism of biosorption should be reemphasized. Uranium is biosorbed as a result of three processes taking place in the cell wall[5]. Initially uranium is complexed by the cell-wall chitin. More uranium ions are adsorbed by the chitin matrix. Hydrolysis of the uranium-chitin complex and deposition of the hydrolysis product containing uranium results in an additional uptake of uranium. All three processes are interrelated; any interference in any of the three processes will affect the overall uranium biosorptive uptake. The largest contribution to uranium uptake is by the second process, adsorption, although all three processes are important.

The results show that at a pH of 2, there is very little effect on the uranium biosorption by any of the competing ions. The effect on the uranium uptake appears to be more a result of the solution pH than the presence of any co-ions. Solution pH affects: 1) hydrolysis of the chitin amine. Low solution pH increases H_3O^+ concentration and intensifies the competition among H_3O^+ and uranium ions for the chitin complexation sites; 2) uranium adsorption, which is a process that depends significantly on the physical and chemical characteristics of the adsorbate. At this low pH, uranyl ions exist in the form of the simple uranyl cations, UO_2^{2+}, whereas at pH > 2.5 it hydrolyses extensively[6] and 3) hydrolysis of the uranium-chitin complex, which is a strong function of pH[5]. Aluminum hydrolyses less below a pH of three[7]. Iron will compete with uranium for complexation by chitin[8]. However, at a pH of 2 iron is present in a simpler form, therefore the presence of iron is overshadowed by the concentration of H_3O^+ ions. The presence of thorium at a pH of 2, as for the other co-ions, does not affect the uranium uptake. The mechanism of thorium uptake consists of a coordination complex between thorium and the cell wall chitin, and adsorption of the hydrolysed thorium ions by the outer

layers of the Rhizopus arrhizus cell wall[9]. At a pH of 2, thorium is not hydrolysed and the competition by H_3O^+ ions strong.

As pH increases, the solubility of uranium decreases. Hence, adsorptivity increases. That is, the higher solution pH favours process B (of the uranium uptake mechanism) by reducing uranium solubility and also favouring uranium complexation by chitin (in the absence of other co-ions).

Earlier studies done on thorium biosorption[9], show that since the majority of thorium biosorbed is due to adsorption of hydrolysed thorium ions by the outer layers of the Rhizopus arrhizus cell wall, the presence of co-ions in solution has an insignificant effect on the overall uptake. Conversely, since the majority of uranium biosorption occurs within the cell wall, the presence of thorium should have an insignificant effect. This is confirmed by the results from the U-Th system (shown in Figure 3.4) for thorium concentrations less than 100 ppm. As the concentration of thorium increases, the system becomes saturated and thorium precipitates, removing uranium from solution. The U-Al-Th system also confirms the "insignificant effect" thorium has on the actual uranium biosorption. In Figure 3.5, the uranium uptake capacity remains essentially the same as the initial thorium concentration increases. However, the uranium uptake capacity is reduced, by the presence of aluminum.

Earlier studies done on uranium biosorption showed that iron competes with uranium for complexation by chitin[5]. The present results confirm this observation (Figure 3.2). A hydrolysis distribution diagram for iron is given in Figure 4.1[10]. At a pH of 4, the total soluble Fe(III) concentration is $10^{-4.16}$ M, and the predominant species is $Fe(OH)_2^+$. The initial iron concentration used in the experiments were $10^{-3.75}$M, $10^{-3.05}$M and $10^{-2.75}$M. Thus it is clear that a large portion of the iron introduced into the system will precipitate in the form of $Fe(OH)_3$. It is quite likely that iron will not only precipitate itself, but the ferric precipitate will also remove uranium from solution.

At a pH of 5, the total soluble Fe(III) concentration is 10^{-3}M; again the predominate species is $Fe(OH)_2^+$. Hence, an even larger amount of iron will precipitate out of the system. Since, the solubility of uranium has also decreased, uranium will also precipitate out.

At a pH of 4, the predominate species of aluminum is Al^{+3}, from the hydrolysis diagram in Figure 4.2[7], the soluble aluminum concentration is $10^{-2.5}$M. The initial aluminum concentration studied ranged from $10^{-3.43}$M to $10^{-2.43}$M. At a pH of 5, the total soluble aluminum concentration is approximately 10^{-5}M. Hence, a majority of the aluminum present will be in the form of the precipitate $Al(OH)_3$. Aluminum does not coordinate readily with nitrogen[11]. It forms strong complexes only with hydroxide and fluoride ligands[7]. Therefore, it is more probable that the aluminum interference is a physical interference.

Aluminum has a complex chemistry. There have been many arguments for monomeric or polymeric hydrolysis schemes, but as noted by Benschoten[12], many arguments are irrelevant, since many experimental results are system specific. The Al speciation is affected by concentration, mixing, type and concentration of anion, and aging[13,14,15]. The divalent sulphate ion is known to affect the course of the hydrolysis-precipitation process as well as the composition, texture and structure of the resulting precipitate. That is, far less alkali is needed to produce visible signs of a precipitate when aluminum is in a sulphate environment than when aluminum is in a chloride or nitrate environment[14]. All of the competitive adsorption isotherms were conducted in a nitrate environment, while the Denison Mine Leachate is essentially a sulphate rich solution. Hence, it is quite likely that the precipitation of aluminum within the chitin infrastructure will be enhanced in a sulphate environment.

4.2 Kinetic Experiments

Using the Carberry reactor system, described in Section 2.4, the effect of aluminum on the kinetics of the uranium uptake by Rhizopus arrhizus was examined. The results showed that although the uranium uptake capacity was reduced, the kinetics of uranium biosorption by Rhizopus arrhizus was not affected. The shape of the kinetic curves (Figure 3.10,3.11) are the same, suggesting that the uranium-nitrogen amine binding sites are not blocked. That is, there is no apparent restriction of access to the chitin sites, only a reduction in the uranium uptake capacity.

An increase in the bulk solution concentration pH also observed (Figure 3.12). It is widely known that chitin will remove hydrogen ions from solution, resulting in an increase not only in the solution pH, but in an even greater increase within the cell wall[16]. With the increase in the pH of the cell wall and the chemistry of the ions, the solubility of each ion will be affected, and hence the adsorptivity of each ion will be affected.

4.3 Electron Microscopy

Two sets of biomass samples were examined using electron microscopic techniques, as outlined in Section 3.3. The results showed that for the CANMET samples, uranium and aluminum are not present, in detectable amounts, in the immobilized biomass particles when iron and thorium are present in significant quantities. It appears that both iron and thorium interfered with the uranium biosorption process by precipitating out onto the biomass, thus blocking access to the chitin sites.

The results from the biosorption isotherm samples confirm that iron precipitates out of solution before adsorbing onto the biomass. It is also quite clear from the aluminum - uranium biosorption isotherms that aluminum interferes with the uranium biosorption process.

4.4 Aluminum Displacement Mechanism

The information discussed in the previous sections allows for the formation of a hypothesis regarding the mechanism of aluminum interference with uranium biosorption by Rhizopus arrhizus; Aluminum interferes with uranium biosorption by the precipitation of an amorphous $Al(OH)_3$. The formation of this precipitate in the cell wall, prevents or severely limits the available space for uranium adsorption.

Supportive evidence for this hypothesis follows:

1) the Al-N bond is not a preferred bond, hence it is unlikely that the reduction of uranium uptake capacity is due to competition of the chitin amine binding sites.

2) the kinetics of uranium biosorption by **Rhizopus arrhizus** appears not to be affected by the presence of aluminum. Uranium is complexed quickly by the cell wall chitin[5]. Competition for complexation by chitin would result in a decrease in the rate of uranium uptake. However, the presence of an amorphous gel that would still allow the diffusion of uranium through to bind with the chitin, would not interfere with the kinetics of uranium biosorption. The initial uranium binding sites would still exist, and further adsorption and deposition of uranium would still occur, but would be reduced, due to the physical limitation resulting from the presence of a metastable amorphous hydroxy polymeric precipitate.

3) Aluminum chemistry shows that aluminum precipitates easily in the pH range 4-5. The precipitation process is enhanced in a sulphate system, similar to the Denison Mine Leachate used in earlier experiments[1,4].

Based on the hypothesis of the aluminum interference on uranium biosorption by **Rhizopus arrhizus**, it was felt that attempting to remove aluminum from the biomass would prove to be difficult, as opposed to using a pretreatment system. Pretreatment could involve removal by adsorption (ion exchange) or the use of chemicals to complex the aluminum out of solution.

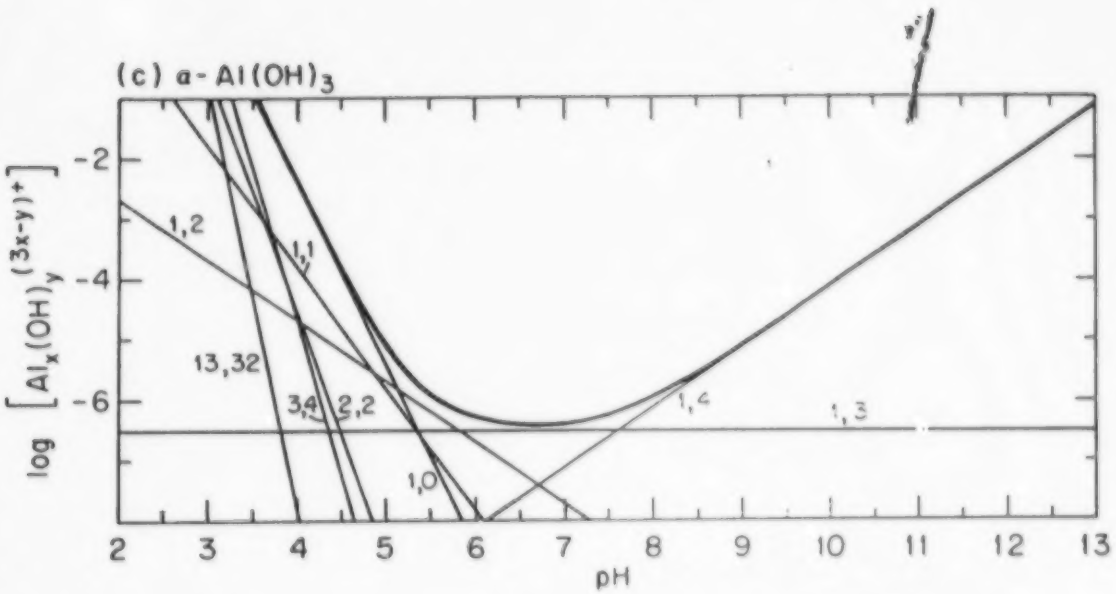


Figure 4.1: Equilibrium concentrations of hydroxo aluminum(III) complexes in a solution saturated with gibbsite.

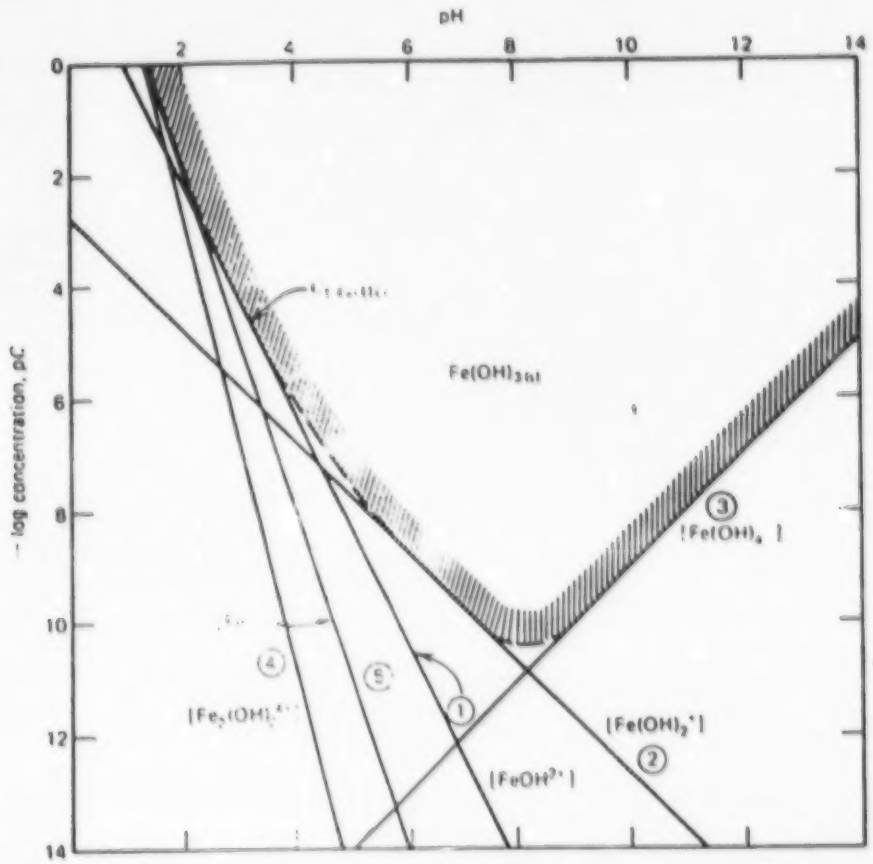


Figure 4.2: Equilibrium concentrations of hydroxo iron(III) complexes in a solution in contact with freshly precipitated $Fe(OH)_{3(s)}$.

5. CONCLUSIONS

The objectives outlined in Section 1.1 have been met successfully. Results from the biosorption equilibrium isotherms, the kinetic experiments and the electron microscopic analysis suggested the following conclusions:

1. Aluminum interferes with the uranium biosorptive uptake capacity of **Rhizopus arrhizus** by the precipitation of a metastable amorphous hydroxy polymeric precipitate. The precipitate limits the space available for uranium adsorption and deposition.
2. Pretreatment of the process solution is suggested, instead of post treatment, as a possible method to alleviate the aluminum interference.
3. The presence of iron and thorium also interfere with the uranium biosorption process, by restricting access to the chitin binding sites, or by precipitating out of solution with uranium.

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Appendix 1:
Competitive Adsorption Isotherms

COMPETITIVE ISOTHERMS-URANIUM AND ALUMINUM					
Test 1: 300 ppm U, 0 ppm Al , pH = 4.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake, mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake, mg/g**
C04-1	16	259	176	1.1	0.45
C04-2	33	232	169	0.92	0.74
C04-3	51	204	162	0.86	0.61
C04-4	70	179	154	0.80	0.52
C04-5	85	133	180	0.58	0.69
C04-6	104	110	171	0.53	0.62
C04-7	150	61	150	0.41	0.51
C04-8	202	20	131	0.33	0.41
Test 2: 300 ppm U, 10 ppm Al. pH = 4.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc, mg/L**	**Aluminum Uptake, mg/g**
C104-1	14	269	134	10	1.8
C104-2	30	247	140	10	1.9
C104-3	51	216	142	10	1.8
C104-4	72	189	138	9	1.7
C104-5	85	175	133	9	1.7
C104-6	96	138	155	9	1.5
C104-7	149	81	138	8	1.4
C104-8	202	45	120	7	1.6
Test 3: 300 ppm U, 25 ppm Al, pH = 4.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C254-1	17	269	120	24	3.1
C254-2	31	252	122	24	3.3
C254-3	52	222	130	23	3.4
C254-4	71	198	129	22	3.3
C254-5	85	182	127	22	3.6
C254-6	101	166	122	21	3.4
C254-7	154	91	128	20	3.0
C254-8	201	58	115	19	3.0

COMPETITIVE ISOTHERMS-URANIUM AND ALUMINUM					
Test 4: 300 ppm U, 50 ppm Al, pH = 4.0					
Flask	**Biomassmg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C504-1	17	268	116	47	3
C504-2	32	249	119	46	4
C504-3	51	228	117	45	4
C504-4	73	199	120	44	5
C504-5	91	178	119	43	5
C504-6	111	132	139	41	5
C504-7	152	94	127	39	5
C504-8	203	64	109	37	5
Test 5: 300 ppm U, 75 ppm Al, pH = 4.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C754-1	16	269	99	69	2.4
C754-2	32	254	100	69	1.8
C754-3	52	230	107	68	3.4
C754-4	69	210	109	67	4.2
C754-5	87	189	111	66	4.9
C754-6	102	176	106	65	4.9
C754-7	153	107	116	62	5.1
C754-8	214	69	101	58	5.3
Test 6: 300 ppm U, 100 ppm Al, pH = 4.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C1004-1	15	271	90	93	6.0
C1004-2	31	257	90	92	6.3
C1004-3	51	237	92	90	6.6
C1004-4	71	214	99	89	6.4
C1004-5	90	193	101	87	8.0
C1004-6	100	184	99	87	7.0
C1004-7	150	115	112	83	7.3
C1004-8	200	79	102	79	7.1

COMPETITIVE ADSORPTION ISOTHERMS-URANIUM AND ALUMINUM					
Test 7: 300 ppm U, 0 ppm Al , pH = 2.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C02-1	15	298	-22	1	-0.15
C02-2	30	287	26	1	-0.02
C02-3	50	272	45	1	0.05
C02-4	70	264	44	1	0.03
C02-5	90	246	53	1	0.02
C02-6	101	242	52	1	0.03
C02-7	151	209	57	1	0.04
C02-8	200	177	58	1	0.04
Test 8: 300 ppm U, 10 ppm Al , pH = 2.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C102-1	15	290	-3	11	-0.93
C102-2	30	281	27	11	-0.43
C102-3	50	269	40	11	-0.18
C102-4	71	255	48	11	-0.10
C102-5	91	242	52	11	-0.04
C102-6	100	236	52	11	-0.06
C102-7	151	203	57	11	-0.01
C102-8	201	174	57	11	0.00
Test 9: 300 ppm U, 25 ppm Al , pH = 2.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C254-1	15	291	-29	27	-4.5
C254-2	31	280	19	26	-1.8
C254-3	51	269	33	26	-1.0
C254-4	70	257	41	26	-0.7
C254-5	91	244	47	26	-0.4
C254-6	101	240	45	26	-0.6
C254-7	150	206	53	26	-0.2
C254-8	201	174	55	26	0.0

COMPETITIVE ADSORPTION ISOTHERMS-URANIUM AND ALUMINUM					
Test 10: 300 ppm U, 50 ppm Al , pH = 2.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Al Conc. mg/L	Aluminum Uptake mg/g
C502-1	15	289	7	51	-5.5
C502-2	30	277	41	51	-0.8
C502-3	51	267	44	51	-0.7
C502-4	70	257	46	51	-1.2
C502-5	91	244	50	51	-0.7
C502-6	101	239	49	51	-0.6
C502-7	150	208	54	51	-0.3
C502-8	200	180	54	51	-0.2
Test 11: 300 ppm U, 75 ppm Al , pH = 2.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Al Conc. mg/L	Aluminum Uptake mg/g
C752-1	15	290	43	73	5.5
C752-2	31	285	38	73	1.5
C752-3	50	279	36	75	-2.9
C752-4	70	263	47	72	1.8
C752-5	90	241	62	72	2.0
C752-6	101	237	59	72	1.2
C752-7	151	207	59	72	0.84
C752-8	200	182	57	72	0.74
Test 12: 300 ppm U, 100 ppm Al , pH = 2.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Al Conc. mg/L	Aluminum Uptake mg/g
C1002-1	15	288	17	98	-2.0
C1002-2	32	282	27	98	-2.8
C1002-3	51	272	38	98	-1.0
C1002-4	71	261	41	98	-0.90
C1002-5	86	243	55	98	-0.95
C1002-6	101	234	56	98	-0.40
C1002-7	151	206	56	97	0.15
C1002-8	201	178	56	97	0.48

COMPETITVE ADSORPTION ISOTHERMS-URANIUM AND ALUMINUM					
Test 13: 300 ppm U, 0 ppm Al , pH = 5.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake, mg/g	Final Al Conc. mg/L	Aluminum Uptake mg/g
C05-1	17	211	353	0.77	0.96
C05-2	30	173	322	0.50	1.41
C05-3	53	109	307	0.36	1.09
C05-4	70	73	282	0.25	0.97
C05-5	85	37	275	0.21	0.85
C05-6	101	18	249	0.15	0.78
C05-7	151	4	177	0.13	0.53
C05-8	203	3	132	0.17	0.38
Test 14: 300 ppm U, 10 ppm Al , pH = 5.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Al Conc. mg/L	Aluminum Uptake mg/g
C105-1	15	228	454	4	40
C105-2	32	188	348	3	24
C105-3	51	134	319	2	17
C105-4	71	90	293	1	13
C105-5	91	45	279	1	11
C105-6	102	33	261	0	9
C105-7	150	5	195	0	6
C105-8	200	3	147	0	5
Test 15: 300 ppm U, 25 ppm Al , pH = 5.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Al Conc. mg/L	Aluminum Uptake, mg/g
C255-1	15	170	812	5	131
C255-2	30	129	540	4	70
C255-3	50	89	405	2	45
C255-4	70	51	345	1	33
C255-5	91	19	302	0	26
C255-6	100	10	282	0	24
C255-7	150	2	194	0	16
C255-8	201	2	145	0	12

COMPETITVE ADSORPTION ISOTHERMS-URANIUM AND ALUMINUM					
Test 16: 300 ppm U, 50 ppm Al , pH = 5.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C505-1	15	73.7	1434	3.8	295
C505-2	31	49.7	793	2.3	152
C505-3	50	25.5	529	0.72	95
C505-4	71	8.4	401	0.11	68
C505-5	90	2.9	320	0.09	54
C505-6	102	1.8	285	0.08	47
C505-7	151	0.79	193	0.12	32
C505-8	201	1.2	144	0.19	24
Test 17: 300 ppm U, 75 ppm Al , pH = 5.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C755-1	15	26	1752	3	456
C755-2	30	18	916	1	237
C755-3	51	5	571	0	143
C755-4	71	1	417	0	103
C755-5	90	1	326	0	80
C755-6	101	0	293	0	72
C755-7	150	1	196	0	48
C755-8	201	0	147	0	36
Test 18: 300 ppm U, 100 ppm Al , pH = 5.0					
Flask	**Biomass mg**	**Final U Conc. mg/L**	**Uranium Uptake mg/g**	**Final Al Conc. mg/L**	**Aluminum Uptake mg/g**
C1005-1	15	19	1820	3	612
C1005-2	30	9	945	1	313
C1005-3	50	3	582	0	191
C1005-4	71	1	416	0	136
C1005-5	90	1	327	0	106
C1005-6	100	0	294	0	96
C1005-7	151	0	195	0	63
C1005-8	200	0	147	0	48

COMPETITIVE ADSORPTION ISOTHERMS: URANIUM AND IRON					
Test 23: 300 ppm U, 0 ppm Fe, pH = 4.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE04-1	15	217	190	0.18	1.07
UFE04-2	30	188	189	0.16	0.60
UFE04-3	50	125	241	0.12	0.44
UFE04-4	70	94	215	0.10	0.34
UFE04-5	91	67	197	0.08	0.29
UFE04-6	101	56	189	0.07	0.27
UFE04-7	150	19	151	0.04	0.20
UFE04-8	201	4	120	0.02	0.16
Test 24: 300 ppm U, 10 ppm Fe, pH = 4.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE104-1	16	210	205	1	53
UFE104-2	31	192	190	1	27
UFE104-3	51	129	240	1	17
UFE104-4	70	100	214	1	12
UFE104-5	91	75	193	1	9
UFE104-6	103	63	182	1	8
UFE104-7	151	26	148	0.6	6
UFE104-8	202	5	121	0.1	4
Test 25: 300 ppm U, 50 ppm Fe, pH = 4.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE504-1	15	225	237	33	112
UFE504-2	30	202	192	32	58
UFE504-3	51	175	168	32	35
UFE504-4	70	121	199	30	28
UFE504-5	91	101	175	29	23
UFE504-6	101	93	167	28	21
UFE504-7	151	61	133	24	17
UFE504-8	202	34	112	20	14

COMPETITIVE ADSORPTION ISOTHERMS: URANIUM AND IRON					
Test 26: 300 ppm U, 100 ppm Fe, pH = 4.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/l	Iron Uptake mg/g
UFE1004-1	15	na	na	na	na
UFE1004-2	33	213	192	86	40
UFE1004-3	50	190	170	85	29
UFE1004-4	71	170	150	85	20
UFE1004-5	93	121	167	82	18
UFE1004-6	103	112	160	81	18
UFE1004-7	153	79	129	76	15
UFE1004-8	201	52	111	70	14

COMPETITIVE ADSORPTION ISOTHERMS-URANIUM AND IRON					
Test 27: 300 ppm U, 0 ppm Fe, pH = 2.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE02-1	15	na			
UFE02-2	31	244.38	38.67	0.33	1.63
UFE02-3	52	230.65	49.70	0.30	1.02
UFE02-4	72	228.38	38.92	0.31	0.72
UFE02-5	90	213.42	47.49	0.32	0.56
UFE02-6	103	204.54	50.35	0.31	0.50
UFE02-7	151	184.62	47.47	0.35	0.32
UFE02-8	209	121.36	64.48	0.36	0.22
Test 28: 300 ppm U, 10 ppm Fe, pH = 2.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE102-1	16	259.06	16.10	11.12	1.18
UFE102-2	30	254.07	24.63	11.18	0.39
UFE102-3	51	241.49	39.67	11.09	0.42
UFE102-4	71	230.26	44.03	10.92	0.53
UFE102-5	91	221.10	44.46	10.88	0.46
UFE102-6	108	214.55	43.41	10.84	0.43
UFE102-7	151	187.30	49.05	10.62	0.45
UFE102-8	206	135.93	60.96	10.00	0.63

COMPETITIVE ADSORPTION ISOTHERMS-URANIUM AND IRON					
Test 29: 300 ppm U, 50 ppm Fe, pH = 2.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE502-1	15	323.89	8.60	50.84	-1.76
UFE502-2	31	312.88	40.24	51.21	-2.10
UFE502-3	50	304.13	42.04	49.10	2.94
UFE502-4	70	291.06	48.69	49.57	1.42
UFE502-5	90	278.10	52.15	48.43	2.37
UFE502-6	101	275.18	49.71	48.71	1.85
UFE502-7	150	241.06	56.01	49.56	0.67
UFE502-8	200	247.54	38.77	56.12	-2.77
Test 30: 300 ppm U, 100 ppm Fe, pH = 2.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE1002-1	16	332	34.59	100.50	-30.67
UFE1002-2	31	328	29.29	94.77	2.78
UFE1002-3	50	314	47.33	94.16	2.91
UFE1002-4	70	303	48.91	94.99	0.90
UFE1002-5	90	290	52.08	94.15	1.63
UFE1002-6	101	286	50.32	95.05	0.56
UFE1002-7	150	253	55.95	94.12	1.00
UFE1002-8	201	230	53.66	94.25	0.68

COMPETITIVE ADSORPTION ISOTHERMS-URANIUM AND IRON					
Test 32: 300 ppm U, 10 ppm Fe, pH = 5.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE105-1	15	210.67	434.82	6.19	63.32
UFE105-2	31	142.91	437.42	5.58	33.55
UFE105-3	50	97.91	355.73	5.12	21.35
UFE105-4	70	57.51	312.06	4.75	15.81
UFE105-5	90	19.19	286.05	12.25	4.02
UFE105-6	101	12.25	262.84	8.04	7.78
UFE105-7	150	5.12	181.15	11.56	2.88
UFE105-8	200	7.75	134.46	18.52	-1.32

COMPETITIVE ADSORPTION ISOTHERMS-URANIUM AND IRON					
Test 33: 300 ppm U, 50 ppm Fe, pH = 5.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE505-1	15	205.37	705.16	16.70	247.20
UFE505-2	30	146.52	548.49	21.79	107.66
UFE505-3	50	108.65	407.60	22.44	63.90
UFE505-4	71	74.56	337.15	20.50	48.05
UFE505-5	90	93.50	243.91	63.42	-9.87
UFE505-6	106	36.76	261.34	18.74	33.81
UFE505-7	151	19.62	195.11	15.42	25.98
UFE505-8	202	9.84	150.43	11.12	21.52
Test 34: 300 ppm U, 100 ppm Fe, pH = 5.0					
Flask	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Fe Conc. mg/L	Iron Uptake mg/g
UFE1005-1	15	200.20	610.00	61.88	195.03
UFE1005-2	31	152.46	463.01	63.21	93.80
UFE1005-3	51	122.65	338.24	64.21	54.64
UFE1005-4	71	91.78	285.81	62.17	42.00
UFE1005-5	90	47.64	272.98	18.35	81.46
UFE1005-6	100	63.65	230.26	61.86	30.02
UFE1005-7	151	36.29	171.33	57.61	22.79
UFE1005-8	203	27.80	131.46	50.63	20.37

COMPETITIVE ADSORPTION ISOTHERMS: URANIUM, ALUMINUM AND IRON							
TEST 35: 300 PPM U, 50 PPM AL, 0 PPM FE, PH = 4							
Sample CADA Series	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc, mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
04-1	15	288	135	40	14	8	-25
04-2	31	182	415	35	23	4	2.3
04-3	50	205	206	37	11	4	0.2
04-4	71	157	214	34	11	3	2.2
04-5	91	132	195	33	10	3	1.7
04-6	101	128	180	32	9	3	1.3
04-7	151	83	150	30	8	3	1.0
04-8	201	48	130	26	8	3	0.6

COMPETITIVE ADSORPTION ISOTHERMS: URANIUM, ALUMINUM AND IRON

TEST 36: 300 PPM U, 50 PPM AL, 10 PPM FE, PH = 4

Sample	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
104-1	15	255	425	36	59	10	21
104-2	31	200	392	34	33	8	16
104-3	50	174	292	33	23	8	10
104-4	71	155	235	32	18	9	7
104-5	90	124	217	30	16	11	3
104-6	100	115	205	29	15	9	4
104-7	150	70	166	26	12	5	5
104-8	200	40	140	23	10	5	4

TEST 37: 300 PPM U, 50 PPM AL, 50 PPM FE, PH = 4

Sample	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
504-1	15	276	203	37	28	42	37
504-2	30	204	338	35	18	40	24
504-3	51	183	244	36	10	40	15
504-4	70	161	206	34	9	39	11
504-5	90	137	187	33	8	34	14
504-6	101	127	178	33	8	34	13
504-7	151	85	147	31	6	31	10
504-8	200	55	125	28	6	28	9

TEST 38: 300 PPM U, 50 PPM AL, 100 PPM FE, PH = 4

Sample	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
1004-1	15	273	281	36	43	78	73
1004-2	30	200	380	34	29	75	46
1004-3	51	171	285	32	21	79	21
1004-4	70	154	229	32	15	73	23
1004-5	90	132	203	31	13	71	20
1004-6	101	128	186	31	12	71	18
1004-7	150	90	149	29	9	67	15
1004-8	200	63	125	27	7	63	13

TEST 39: 300 PPM U, 50 PPM AL, 0 PPM FE, PH = 2							
Sample CADA Series	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
02-1	15	295	22	44	-4	3	-5
02-2	30	284	46	43	1	1	3
02-3	50	272	52	43	1	1	1
02-4	70	264	49	43	0	1	1
02-5	90	249	55	42	0	1	0
02-6	101	245	53	43	0	1	0
02-7	151	175	82	43	0	1	0
02-8	201	146	76	42	0	1	0
TEST 40: 300 PPM U, 50 PPM AL, 10 PPM FE, PH = 2							
Sample CADA Series	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
102-1	15	291	62	43	0.30	12	8.4
102-2	30	287	42	43	-0.80	12	3.5
102-3	50	276	49	43	0.00	12	2.8
102-4	70	270	43	43	-0.42	12	1.9
102-5	90	257	48	43	0.06	12	1.3
102-6	101	253	46	43	-0.02	12	1.2
102-7	151	187	74	44	-0.71	12	0.64
102-8	200	157	71	43	-0.20	11	0.96
TEST 41: 300 PPM U, 50 PPM AL, 50 PPM FE, PH = 2							
Sample Series	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
502-1	16	307	-11	43	-1.07	43	6
502-2	30	301	13	43	-0.76	42	6
502-3	51	295	19	43	-0.94	42	3
502-4	70	283	30	43	-0.28	41	4
502-5	91	275	33	43	-0.63	41	3
502-6	101	267	38	42	0.04	40	4
502-7	151	244	40	43	-0.22	40	2
502-8	200	179	62	42	-0.02	38	2

TEST 39: 300 PPM U, 50 PPM AL, 0 PPM FE, PH = 2

TEST 42: 300 PPM U, 50 PPM AL, 100 PPM FE, PH = 2

Sample CADA series	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
1002-1	15	315	1	43	-2.16	85	-10
1002-2	31	310	14	43	-1.62	84	-3
1002-3	51	300	28	43	-0.90	84	-2
1002-4	71	289	36	42	-0.21	84	-0.7
1002-5	90	280	38	43	-0.65	84	-1
1002-6	101	281	33	44	-1.38	84	-0.7
1002-7	151	251	41	43	-0.78	83	-0.2
1002-8	200	185	64	43	-0.42	82	0.4

COMPETITIVE ADSORPTION ISOTHERMS: URANIUM, ALUMINUM AND IRON

TEST 43: 300 PPM U, 50 PPM AL, 0 PPM FE, PH = 5

Sample CADA Series	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/g	Al Uptake mg/g	Final Fe Conc.mg/ L	Fe Uptake mg/g
05-1	16	24	386	0.31	110	1.6	15
05-2	31	11	243	0.18	57	1.1	9
05-3	51	4	160	0.20	34	1.4	5
05-4	71	2	117	0.14	24	1.2	3
05-5	91	2	91	0.16	19	1.4	2
05-6	104	2	80	0.15	16	2.8	1
05-7	151	2	54	0.25	11	1.7	1
05-8	205	2	40	0.276	8	0.5	1

TEST 44: 300 PPM U, 50 PPM AL, 10 PPM FE, PH = 5

Sample CADA Series	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
105-1	16	15	1310	0	310	3	72
105-2	32	4	676	0	152	2	38
105-3	51	2	424	0	94	2	23
105-4	73	2	295	0	65	3	15
105-5	91	2	237	0	52	3	12
105-6	104	4	206	0	46	6	7
105-7	158	6	134	0	30	10	2
105-8	203	3	106	0	23	4	5

COMPETITIVE ADSORPTION ISOTHERMS: URANIUM, ALUMINUM AND IRON							
TEST 45: 300 PPM U, 50 PPM AL, 50 PPM FE, PH = 5							
Sample CADA Series	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
505-1	16	35	1359	2	300	12	254
505-2	30	27	722	1	155	10	135
505-3	50	17	453	1	94	8	85
505-4	70	12	333	1	68	7	63
505-5	91	8	261	1	52	5	50
505-6	102	9	231	1	47	10	40
505-7	152	2	160	0	31	2	32
505-8	201	6	118	0	23	11	20
TEST 46: 300 PPM U, 50 PPM AL, 100 PPM FE, PH = 5							
Sample CADA Series	Biomass mg	Final U Conc. mg/L	U Uptake mg/g	Final Al Conc. mg/L	Al Uptake mg/g	Final Fe Conc. mg/L	Fe Uptake mg/g
1005-1	15	56	1507	2	306	39	402
1005-2	33	43	740	2	144	34	202
1005-3	50	37	496	2	94	33	134
1005-4	71	30	363	2	67	31	99
1005-5	90	28	286	1	52	31	76
1005-6	101	25	258	1	47	29	71
1005-7	150	18	178	1	31	21	52
1005-8	200	12	136	1	23	15	42

COMPETITIVE ADSORPTION ISOTHERMS: URANIUM, THORIUM SERIES					
TEST 47: 300 ppm U, 0 ppm Th, pH = 4					
Sample	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Th Conc. mg/L	Thorium Uptake mg/g
UTH04-1	16	259	191	0	-2
UTH04-2	30	225	212	0	1
UTH04-3	50	166	245	1	-1
UTH04-4	72	122	233	0	1
UTH04-5	90	62	252	-1	1
UTH04-6	105	37	242	1	-1
UTH04-7	151	14	182	1	-1
UTH04-8	207	11	134	2	-1

COMPETITIVE ADSORPTION ISOTHERMS: URANIUM, THORIUM SERIES					
TEST 48: 300 ppm U, 50 ppm Th, pH = 4					
Sample		Final U	Uranium	Final Th	Thorium
UTH504-1	16	222	423	2	282
UTH504-2	33	194	288	2	134
UTH504-3	53	148	261	2	82
UTH504-4	75	74	285	4	56
UTH504-5	94	44	259	2	47
UTH504-6	105	34	241	2	41
UTH504-7	151	10	184	4	28
UTH504-8	200	8	139	4	21
TEST 49: 300 ppm U, 100 ppm Th, pH = 4					
Sample	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Th Conc. mg/L	Thorium Uptake mg/g
UTH1004-1	16	187	667	3	530
UTH1004-2	31	162	439	2	285
UTH1004-3	51	126	333	2	170
UTH1004-4	70	72	321	4	121
UTH1004-5	87	48	286	3	100
UTH1004-6	103	26	262	3	83
UTH1004-7	153	5	190	5	55
UTH1004-8	201	5	145	6	42
TEST 50: 300 ppm U, 200 ppm Th, pH = 4					
Sample	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Th Conc. mg/L	Thorium Uptake mg/g
UTH2004-1	15	189	767	34	1269
UTH2004-2	31	168	426	11	671
UTH2004-3	50	152	298	2	435
UTH2004-4	71	124	249	-1	311
UTH2004-5	93	75	243	-3	239
UTH2004-6	102	64	232	-3	218
UTH2004-7	156	14	184	-2	142
UTH2004-8	205	2	146	0	107

COMPETITVE ADSORPTION ISOTHERMS: URANIUM AND THORIUM					
TEST 51: 300 ppm U, 50 ppm Th, pH = 2					
Sample	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Th Conc. mg/L	Thorium Uptake mg/g
UTH502-1	15	291	16	56	-2
UTH502-2	32	293	2	50	17
UTH502-3	51	281	25	42	27
UTH502-4	74	273	27	21	47
UTH502-5	88	278	18	-4	68
UTH502-6	103	253	39	-4	58
UTH502-7	127	226	53	-7	49
UTH502-8	204	187	52	-5	30
TEST 52: 300 ppm U, 100 ppm Th, pH = 2					
Sample	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Th Conc. mg/L	Thorium Uptake mg/g
UTH1002-1	14	298	-9	87	89
UTH1002-2	31	299	-7	80	66
UTH1002-3	51	292	9	70	59
UTH1002-4	70	286	16	63	52
UTH1002-5	90	280	19	51	55
UTH1002-6	106	275	21	39	58
UTH1002-7	150	244	35	9	61
UTH1002-8	201	218	39	1	49
TEST 53: 300 ppm U, 200 ppm Th, pH = 2					
Sample	Biomass mg	Final U Conc. mg/L	Uranium Uptake mg/g	Final Th Conc. mg/L	Thorium Uptake mg/g
UTH2002-1	17	338	11	174	158
UTH2002-2	31	338	6	165	111
UTH2002-3	51	310	58	158	83
UTH2002-4	72	290	69	141	82
UTH2002-5	86	299	48	137	73
UTH2002-6	103	292	46	125	73
UTH2002-7	149	281	39	101	66
UTH2002-8	203	268	36	65	67

PRECISION ANALYSIS FOR UPTAKE CAPACITY TEST 31: 300 PPM U, PH = 4					
FLASK	BIOMASS	FINAL U CONC.	U UPTAKE	MEAN Q	STD DEV
UED4-1	0.0710	61.31	361.17	361.4939	0.104484
UED4-2	0.0711	58.53	364.58		9.534372
UED4-3	0.0710	58.83	364.67		10.08286
UED4-4	0.0713	60.35	361.00		0.244796
UED4-5	0.0710	62.39	359.65		3.401687
UED4-6	0.0719	60.39	357.92		12.72584
UED4-7	0.0727	58.83	356.14		28.64281
UED4-8	0.0709	57.65	366.84		28.6231
				STD DEV=	13.33714

95% CONFIDENCE LIMITS= QBAR-T*S/SQRTN=361.5-2.31*13.3/SQRT8=10.86
RANGE=6.75
SAMPLE SIZE=8

THIS IS PLUS OR MINUS 3 % OF THE MEAN

Appendix 2:
Kinetic Experiments

ALUMINUM AND URANIUM KINETIC EXPERIMENTS			
EXPERIMENT ONE: URANIUM ONLY (500 PPM)			
SAMPLE	TIME MINUTES	U FINAL CONC MG/L	U UPTAKE MG/G
KUEXP-1	2	386	227
KUEXP-2	5	390	219
KUEXP-3	10	380	239
KUEXP-4	15	384	229
KUEXP-5	20	391	216
KUEXP-6	25	385	228
KUEXP-7	30	387	223
KUEXP-8	45	384	229
KUEXP-9	60	369	258
KUEXP-10	120	369	257
KUEXP-11	240	361	272
KUEXP-12	540	351	292
KUEXP-13	1185	331	330
KUEXP-14	1440	327	338
KUEXP-15	1680	332	328
KUEXP-16	3140	323	343
KUEXP-17	4320	321	348
KUEXP-18	5880	321	347
KUEXP-19	7270	315	357
KUEXP-20	8640	324	339
KUEXP-21	10095	316	355
KUEXP-22	11580	318	350

ALUMINUM AND URANIUM KINETIC EXPERIMENTS					
EXPERIMENT TWO: 500 PPM URANIUM, 500 PPM ALUMINUM					
SAMPLE	TIME MINUTES	U FINAL CONC MG/L	U UPTAKE MG/G	AL FINAL CONC MG/L	AL UPTAKE MG/G
K1114-1	0	493	0	463	0
K1114-2	1	489	7	458	10
K1114-3	1	485	17	454	17
K1114-4	3	482	22	456	14
K1114-5	5	481	24	460	7
K1114-6	10	473	40	456	14
K1114-7	15	465	56	452	23
K1114-8	20	466	54	457	12
K1114-9	25	462	61	455	15
K1114-10	30	463	60	459	9
K1114-11	45	461	63	459	7
K1114-12	60	455	74	456	14
K1114-13	120	448	88	458	10
K1114-14	240	441	102	455	15
K1114-15	570	434	116	454	18
K1114-16	1320	432	119	458	10
K1114-17	1740	429	125	457	11
K1114-18	2790	430	122	460	7
K1114-19	4440	426	129	459	8
K1114-20	6260	429	124	462	2
K1114-21	7440	422	136	457	12
K1114-22	8700	427	127	459	8
K1114-23	10390	428	126	459	8
K1114-24	11927	423	135	455	16

PH VALUES FOR KINETIC RUNS '90			
EXPERIMENT ONE: URANIUM ONLY (500 PPM INITIALLY)		EXPERIMENT TWO: URANIUM AND ALUMINUM (U-AL-500 PPM INITIALLY)	
TIME MINUTES	PH	TIME MINUTES	PH
0	3.99	0	4.00
5	4.02	5	4.05
10	4.03	10	4.08
15	4.00	15	4.10
20	4.00	20	4.10
25	4.10	25	4.15
30	4.10	30	4.17
45	4.10	45	4.25
60	4.20	60	4.41
120	4.18	120	4.43
240	4.09	220	4.34
360	4.07	570	4.17
690	4.00	1260	4.09
1320	3.94	1620	4.08
1860	4.00	2880	4.04
3180	3.95	4320	4.02
4500	3.93		